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PHOTODEGRADATION OF FIVE ORGANOPHOSPHORUS INSECTICIDES  
ON GLASS AND LEAF SURFACES

by

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## INTRODUCTION

During the past two decades there has been an unprecedented increase in the number and use of synthetic organic insecticides. Great concern has been expressed over environmental contamination by insecticides of soil, water, and plant and animal life. Investigations have been conducted on insecticide residues, their persistence in the environment, and the conversion of these compounds to other toxic and non-toxic degradation products. However, little is still known about many aspects of these insecticides in regard to their persistence or disappearance. The effects of environmental factors including air movement, water vapor in the air, free water on leaf surfaces, temperature, and solar radiation on the fate of insecticides needs to be extensively investigated.

Solar radiation is one of the most important considerations when examining the fate of surface deposits of insecticides. The sun is the greatest source of energy, and energy is the needed requirement for many of the chemical degradation reactions of insecticides. The irradiation of the sun can provide the necessary energy needed to break chemical bonds and form new compounds. Information is needed in the area of insecticide photochemistry, if we are to completely understand the fate of insecticide surface residues.

The objectives of the present research were: (1) to determine the effects of specific regions of the electromagnetic spectrum (infrared, solar visible region, and near and far ultraviolet light) upon the deposits of parathion, methyl parathion, malathion, Guthion and diazinon when applied to leaf surfaces and to glass plates; (2) to examine the irradiated insecticide deposits on glass and leaf surfaces at various time intervals

after application and to determine the degradation products comprising the insecticide residue.

## REVIEW OF LITERATURE

### Photochemistry Theory and Photochemical Reactions

The electromagnetic spectrum or "light", is an orderly arrangement of radiant energy according to wavelength and frequency, and extends from very long-wave, low-energy photons of the radio region, as produced by oscillatory electrical circuits, to the extremely high-energy particles of the short-wave cosmic and ultraviolet rays. This is illustrated in Fig. 1 of Plate I. The dual nature of electromagnetic radiation is well established (White, 1962). Light acts like both a particle and a wave and is apparently a stream of particulate matter which are called photons (Rodebush and Rodebush, 1945). These photons may have widely varying energy levels but all photons travel at the same speed, the speed of light. The energy possessed by a photon is related to its wavelength by the following equation:

$$E = h \nu$$

E is the energy in ergs of one photon,  $h$  is a universal constant called Plank's constant ( $6.624 \times 10^{-27}$  erg seconds), and  $\nu$  is the frequency of the radiation in vibrations per second (Rollefson and Burton, 1947). It is seen that the energy associated with electromagnetic radiation is inversely proportional to the wavelength and directly proportional to the frequency (number of vibrations per second), which is to say that ultraviolet radiation having a shorter wavelength than visible light, has a

greater amount of ready energy than visible light. Infrared radiation has a longer wavelength than visible and thus is less energetic (Brewster and McEwen, 1963).

Atoms at room temperature have most of their electrons in the ground state, and this is represented by the expression  $E_0$ ; a state of minimum energy. If a photon of the proper energy passes near the atom it may be absorbed. The energy of the photon is transferred to the atom, the atom passes from a low-energy ground state ( $E_0$ ) to a so called excited state. This absorption of energy will involve only the valence, or outer most electrons of the atom (Reid, 1957). Jagger (1967) stated that usually only one electron is the recipient of the incoming energy. There are possible a number of excited states that an electron may exhibit and these states or levels require varying degrees of energy. A particular energy jump is known as a transition, and a transition from a lower to higher level of energy requires a discrete amount of energy. An energy level diagram for an atom is presented in Fig. 2 of Plate I. If an electron is raised to second excited state ( $E_2$ ) it may not fall back to the ground state in a single act, but may instead fall first to the first excited state ( $E_1$ ) and then to the ground state ( $E_0$ ). This fluorescence will involve the emission of two photons, both of lower energy than the exciting photon. If an electron absorbs a photon and is raised to the first excited state, it may almost immediately fall back to the ground state ( $E_0$ ), but with the concomitant emission of a photon. In the absence of complicating factors, the emitted photon will have exactly the same energy as the exciting photon ( $E_1 \longrightarrow E_0$ ). The Pauli Principle as stated by White (1962) says that in an atom in a stable state, no two electrons can have

## EXPLANATION OF PLATE I

Fig. 1. The diagramatic representation of the electromagnetic spectrum.

Fig. 2. The energy level diagram of an atom.

- (1). Absorption of a photon by an electron resulting in an increase in energy level from the ground state to the first excited state.
- (2). Emission of a photon by an electron resulting in a decrease in energy level from the first excited state to the ground state. (fluorescence).
- (3). Photon whose energy exceeds the ionization potential excites the electron which then escapes from the atom causing the atom to become ionized.
- (4). Absorption of a photon by an electron resulting in an increase in energy level from the ground state to the second excited state.
- (5). Emission of a photon by an electron resulting in a decrease in energy level from the second excited state to the first excited state and then to the ground state.
- (6). Emission of a photon by an electron from the second excited state to the first excited state and from the first excited state to the ground state involving the emission of two photons, both of lower energy than the exciting photon. (fluorescence).
- (7). Delayed emission of a photon from the triplet state to the ground state. (phosphorescence).

# PLATE I

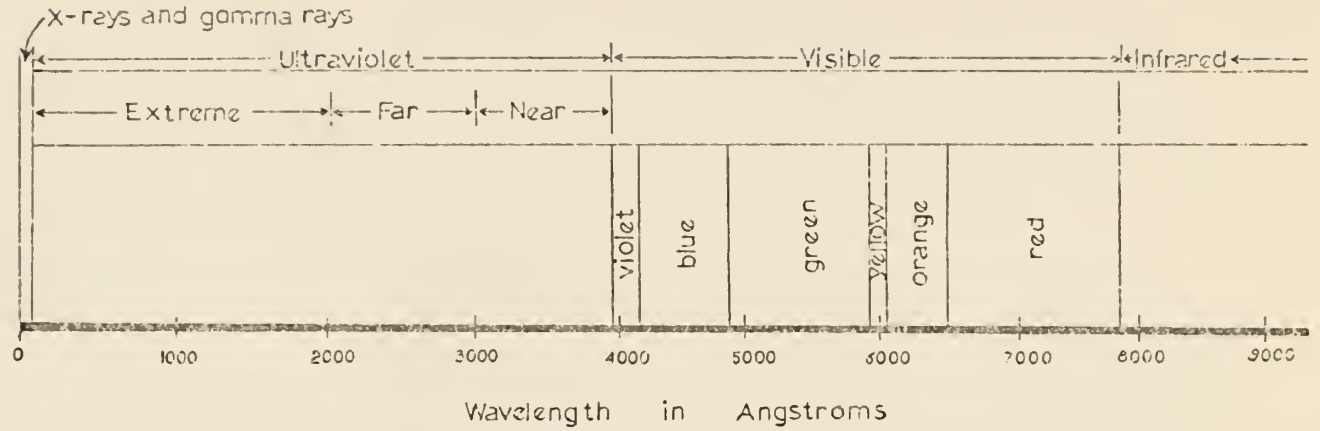


Fig. 1. The Electromagnetic Spectrum

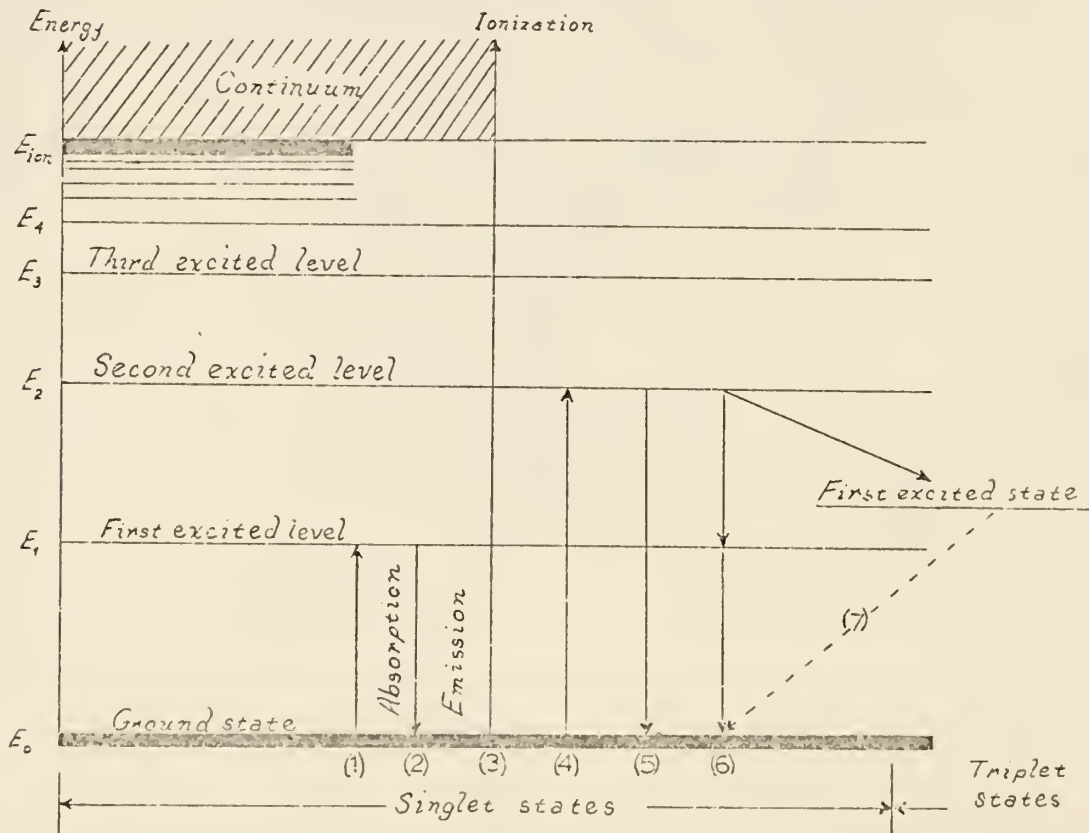


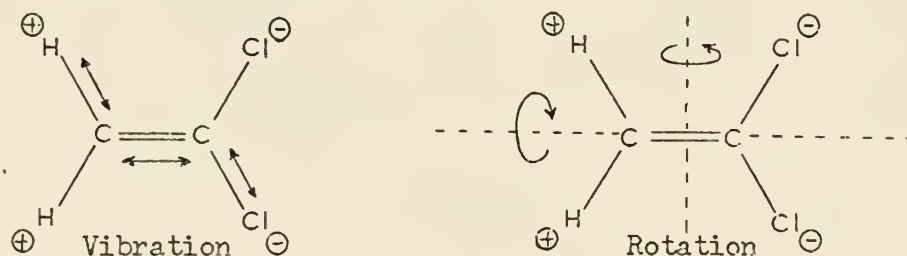
Fig. 2. Energy Level Diagram

exactly the same energy. Two electrons can manage to have the same energy in all respects except for the spin of their orbitals, and for this reason, electrons in atoms form pairs having virtually equal energies though opposite spins. If an electron will reverse its spin so that it is parallel to that of its neighbor valence electron a condition will exist which will cause the atom to enter the triplet state. This state has a whole different arrangement of energy levels from that of normal atoms which are in the singlet state. The triplet state has no ground level and transition from the triplet first state to the singlet ground state is not very probable. Electrons become trapped in the triplet state and remain in this excited state for relatively long times. The processes of emission or absorption normally take place in about a thousandth of micromicrosecond ( $10^{-15}$  sec) and isolated atoms will usually remain in an excited state for about  $10^{-8}$  second. In the triplet state an electron may remain in that state for as long as a second before it drops down to the ground state and emits a photon. This delayed emission of a photon is called phosphorescence (Margenau, 1950).

The levels of the electron excited states come closer together the higher one goes with respect to the ground state energy level. A limit is reached when the energy levels merge into a continuum, which does not possess discrete energy levels. The lower limit of the continuum requires a level of energy called the ionization energy ( $E_{ion}$ ). The ionization potential of an atom is the difference between the ionization energy and the ground state energy (Shirley, 1964). If a photon possesses less energy than the ionization potential, it can excite an electron only if it has just the right energy to raise it to the per-

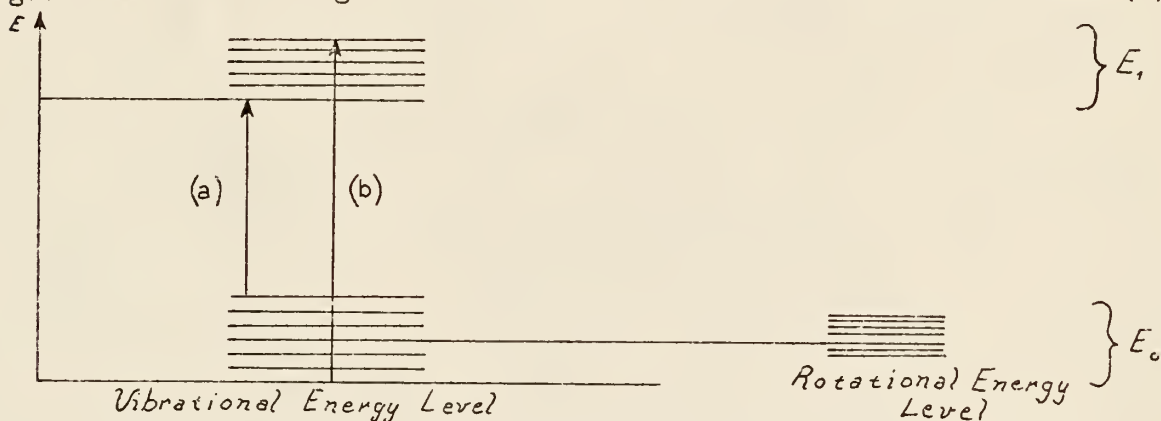
mitted level, and this accounts for the discrete absorption spectra of atoms. Any photon whose energy exceeds the ionization potential may excite the electron causing it to escape and the atom is ionized (Hollaender, 1954).

Synthetic organic compounds are comprised of chemically combined atoms called molecules. Organic molecules upon exposure to photon irradiation undergo the same reactions as an atom, and will also do some things which atoms can not do. In an organic molecule the valence electrons of constituent atoms are usually shared to some extent with one or more other atoms in the molecule and are referred to as molecular electrons (Jagger, 1967). There is only one type of motion an atom can undergo and that is translation. A molecule can also undergo translation, but in addition can undergo two types of motion, vibrational and rotational. This type of motion is illustrated by the dichloro-ethylene molecule. The C-H and C-Cl groups can vibrate along their axis, and



this vibration alters the bond length, hence the energy required for the associated electron to reach an excited state is reduced. There could also be vibrations of C=C bond along its axis and of the C-H and C-Cl bonds with respect to one another. Jagger (1967) stated that vibrational energy changes are usually much smaller than electronic energy changes and that low-energy photons in the infrared region of the electromagnetic spectrum can cause a transition of vibrational state with no change in the electronic configuration. The following diagram

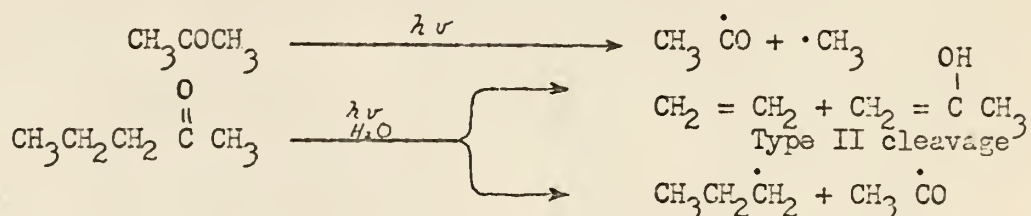
illustrates how a molecule in the electronic ground state, but in an energetic vibrational level could be excited to an electronic first state of low vibrational energy by a photon of lower energy (a) than would be required for excitation from a low vibrational level in the ground state to a high vibrational level in the first excited state (b).



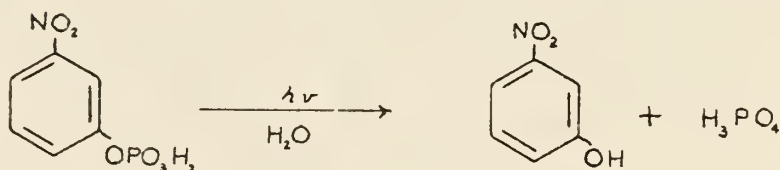
Rotational energy in the dichloro-ethylene molecule can cause rotation about the C=C double bond axis or about an axis at right angles to this. Parker (1964) states that energy changes involved in rotation are so small that they merely represent perturbation of the vibrational levels of a molecule. Shirley (1964) mentioned that energies of molecular rotation and vibration are usually confined to the infrared region and energies of electronic excitation occur in the infrared, visible and especially in the ultraviolet region of the light spectrum.

A molecule after it has absorbed a photon does not immediately re-emit a photon of the same energy. Other processes usually intervene causing the electronic excitation energy to become directly utilized, stabilized, degraded or transferred (Hollaender, 1954). Direct utilization of the excitation energy by a molecule usually causes chemical change such as a bond breakage or oxidation and reduction reactions (Margenau, 1950). Weissberger (1956) reported that frequent irradiation leads to dissociation of the absorbing molecule. The species produced

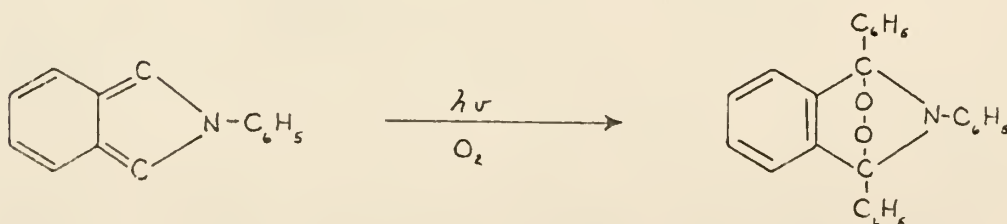
may be radicals, ions, carbenes or small molecules. Pitts (1957) and Noyes, Porter and Jolley (1956) studied the photochemical reactions of aldehydes and ketones in the vapor phase. Molecule cleavage to radicals and, if a  $\gamma$ -hydrogen atom was present, the so-called type II process were both observed.



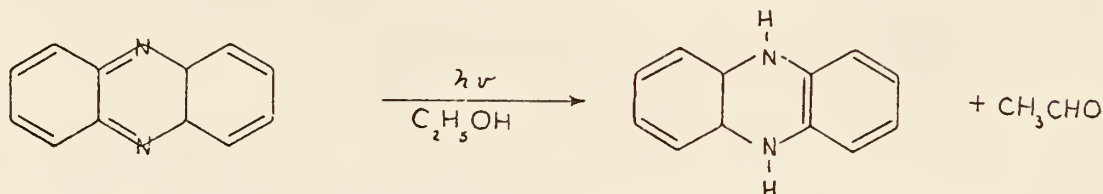
Havinga (1956) has shown that there is an unexpected substituent effect in the photoirradiation of *m* and *p*-nitrophenyl phosphates. Irradiation of the meta compound results in relatively fast hydrolysis, whereas the para substituted compound shows little or no photodissociation.



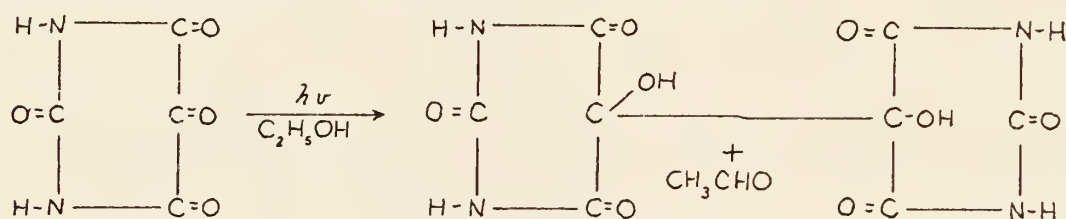
Thielacker and Schmidt (1957) studied the oxidation of a solution of 1,2,3-triphenyl isoindole upon photoirradiation. The photooxidation product of 1,2,3-triphenyl isoindole was 1,2,3-triphenyl isoindole peroxide.



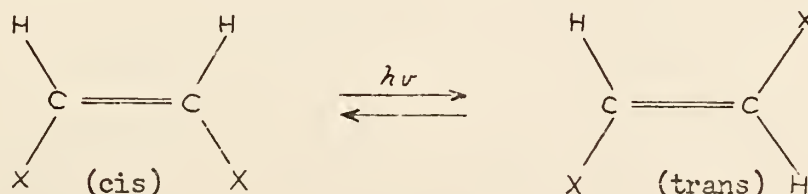
Dufraisse, Eteinne and Toromanoff (1952) studied the effect of photoirradiation on phenazine in an ethanol solution. They found the photochemical reduction product was dihydrophenazine.



Ciamician and Silber (1903) found the photoreduction product of alloxan in a solution of ethanol to be alloxantin.



Stabilization of energy such as exhibited by a cis-trans molecular change is a way that energy is held for latter use. This switching of a molecule into a meta-stable state can cause a very temporary stabilization of energy. Irradiation of many compounds containing olefinic linkages results in isomerization as in the following reaction which was studied by Wyman (1955). He stated that in simple systems it frequently occurs that the trans isomer absorbs light in the infrared or long wavelength more intensely than the cis isomer: the mixture usually reaches a photostationary state in which the less stable cis isomer predominates at equilibrium.



Transfer of energy within a molecule is chiefly of the kind called delocalization. Molecular conjugated structures are responsible for most organic absorption of short-wave irradiation (Jagger, 1967). Benzene and other conjugated structures absorb photons as a unit, the whole absorbing unit being called a chromophore (Day and Underwood, 1962). If there is a substituted group at some point adjacent to the ring, and if the group possesses a weak bond, then the energy absorbed by the chromophore will first excite the whole chromophore and will then be drained off into the weak bond which will be broken. Delocalization is not common because excitation energy can not just run along a molecular chain. It can only travel through the regions of the molecule where there is an overlap of electron orbits (Shirley, 1964).

There are several ways for intermolecular transfer of energy to occur. One method of transfer is known as resonance transfer. It may involve either two different molecules or two different parts of the same molecule. The resonance excitation mechanism will occur over distances considerably greater than molecular diameters (Bennet, 1964). Ware (1961) stated that resonance mechanisms were insensitive to the viscosity of the solvents in which they were placed. In crystalline materials, intramolecular transfer can occur by a charge conduction. This is the process which occurs when electricity is conducted through a copper wire.

In conclusion it should be mentioned that there is one organic photochemical reaction which is obviously older than man and is of great economic as well as chemical importance. The reaction is the photochemical mechanism of plants and is called photosynthesis.

There are many photochemical reactions which were not investigated in the foregoing review of literature. Many photochemical reactions were not listed because of their high degree of specificity, and their lack of simple or general reaction mechanisms which could be applied to many compounds and not just those of a specific nomenclature.

### Organic Phosphorus Insecticides

In the past twenty years synthetic organic phosphorus insecticides have assumed an increasingly important role in agricultural practice. Their increased usage and subsequent misuse has prompted much research and investigation into their overall effectiveness. The lack of stability in the presence of light has complicated the problem of determining the effectiveness and safety of the organic phosphorus insecticide compounds.

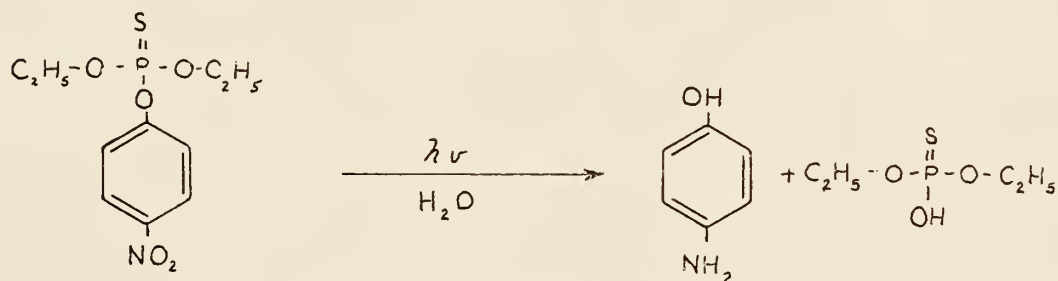
Reports of various researchers evidence the interest in the effects of light upon the insecticidal properties of the organic phosphorus insecticides. It was reported by Frawley et al. (1958) that exposing parathion spray deposits to ultraviolet light resulted in a residue mixture of compounds showing greater in vitro anticholinesterase activity than parathion but lower reactivity to the Averell-Norris (1948) chemical analytical method and a lower toxicity to flies. Payton (1953) found that when emulsions of parathion in aqueous salt solutions were exposed to ultraviolet light (1850-4000 Å) the emulsions developed anticholinesterase activity. This activation occurred first at room temperature in emulsions and solutions exposed to daylight. Anticholinesterase activation did not occur when solutions were placed in the dark or when they were exposed to an electric incandescent light

source. Cook and Ottens (1959) studied several organic phosphate insecticides, (trithion, ethion, Thimet, and malathion) and found that these insecticides when spotted on paper and exposed to ultraviolet light are converted very quickly to compounds which were less polar than the parent compound. Short periods of exposure to germicidal lamps converted small quantities (2-4 ug) of the insecticides almost completely to less polar compounds. On prolonged exposure to ultraviolet irradiation a series of more highly polar compounds were formed. The authors stated that this same phenomenon took place on paper, glass and leaf surfaces upon exposure to sunlight. They noted this conversion also took place with Guthion and parathion but at a very slow rate. El-Refai (1960) also investigated the effects of ultraviolet light and other weathering factors on the qualitative and quantitative losses of malathion residues. He employed two types of substrates for the residue study, glass and glass plates coated with alfalfa wax. Numerous breakdown products occurred and were isolated and identified following ultraviolet irradiation. The most interesting metabolite isolated was malaaxon.

Mitchell (1961) exposed many paper chromatographed organophosphorus insecticides to various light sources. The light sources consisted of: (1) daylight; (2) long wave ultraviolet light 3660 Å (the so-called black light); (3) short wave ultraviolet light 2537 Å. The irradiated chromatograms were developed and the results interpreted. He found extensive decomposition of the organophosphorus compounds had occurred after exposure to the shortwave ultraviolet light. Some of the decomposition products were the oxygen analogs of the parent organophosphorus insecticides.

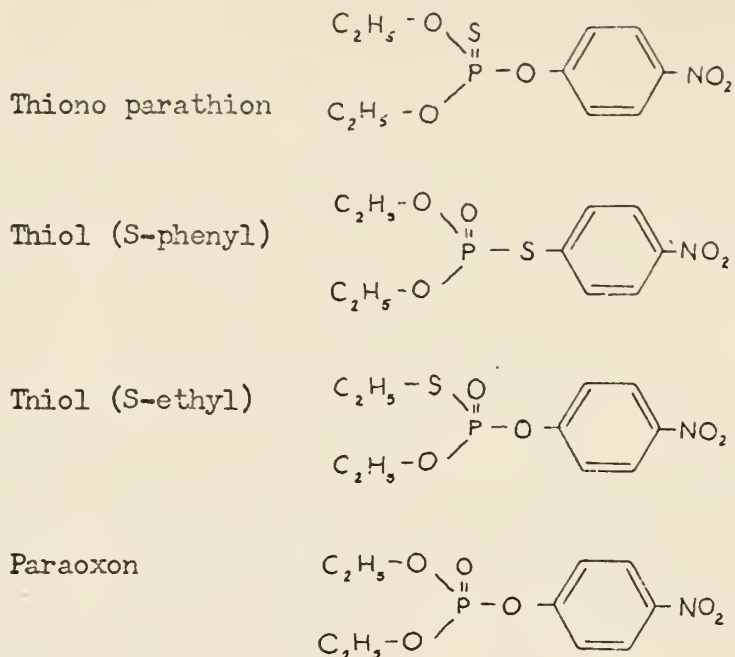
Cook (1954) discovered that the isomers of Systox, when exposed to air and light on paper chromatograms, are converted quite readily to other compounds, and these photoconversion products are more hydrophilic than their parent compounds. The Systox isomer was not changed into a cholinesterase (ChE) inhibitor, but the photoconversion product from Isosystox was a strong ChE inhibitor like its parent compound. Infrared absorption spectra indicated that the conversion product from Systox retained a P=O linkage. Cook concluded that the change in the molecules from exposure to light must be at some other linkage other than the P=S or P=O.

Sandi (1958) showed that the photochemical hydrolysis of parathion by ultraviolet light resulted in the production of the corresponding p-amino compound being formed, p aminophenol.



Cook and Pugh (1957) investigated the ChE-inhibiting decomposition products of parathion, its sulfur isomers (thiol S-phenyl, thiol S-ethyl) and oxygen analog which were formed by the action of ultraviolet light, and found that these compounds were about equally potent as anti-ChE agents.

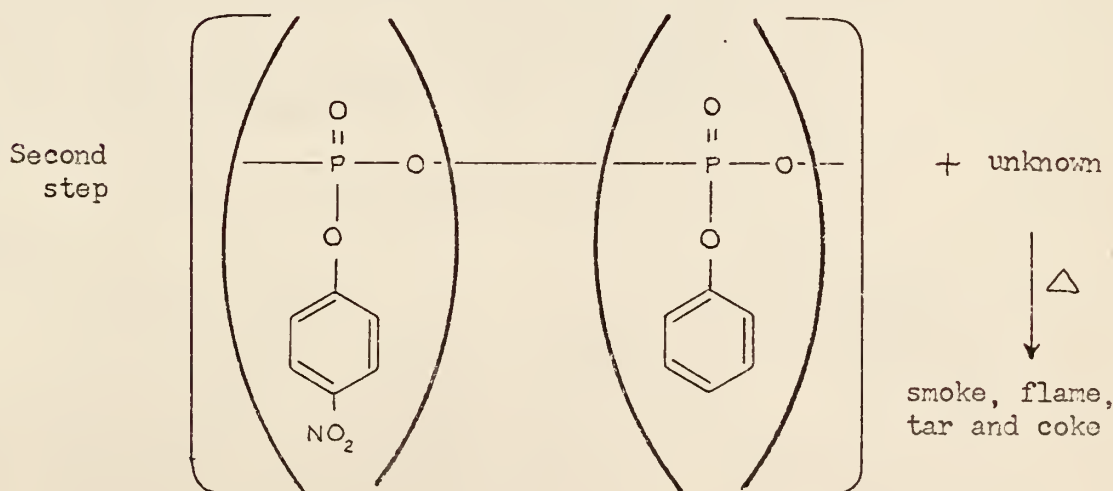
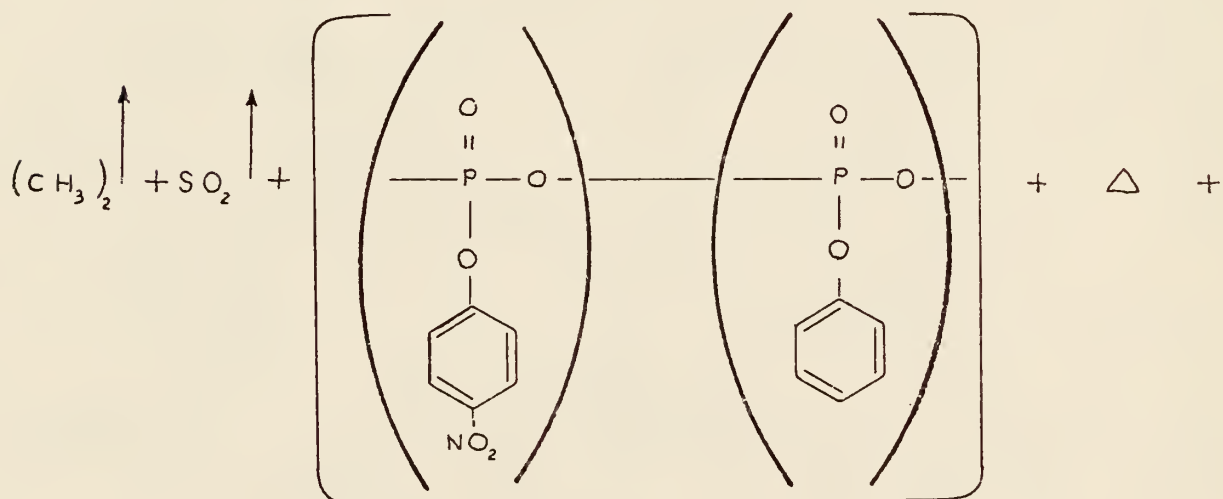
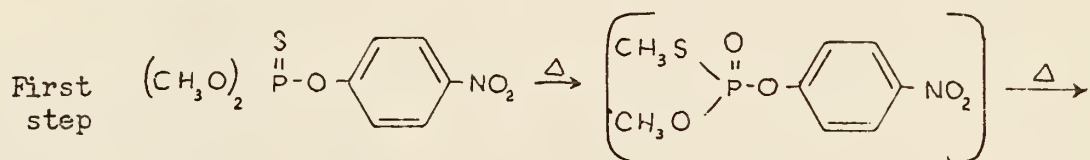
Cook (1955) studied twelve organophosphorus insecticides and their conversion to in vitro cholinesterase inhibitors by N-bromo-succinimide and ultraviolet irradiation. He found a number of thiophosphate insecticides were converted to more potent cholinesterase inhibitors. The com-



pounds formed were relatively more soluble in water than in oil when compared to the parent compounds.

Metcalf and March (1953) have found that parathion and its methyl homolog isomerize readily upon heating to 150°C, and at least in the case of methyl parathion, by exposure to ultraviolet light. The heat isomerization products were a mixture of compounds of which the S-alkyl isomerides were the chief constituents. They also stated that malathion and EPN undergo similar heat isomerization at 150°C. Casida (1956) also reported that the phosphorothioates isomerize to more active antiesterase agents in the presence of heat or ultraviolet light. This isomerization with dialky p nitrophenyl phosphorothioates yields S-alkyl derivatives. However, with O,O-diethyl and O,O-dimethyl O-ethyl-2 mercaptoethyl phosphorothionates and O,O-diethyl O-B-diethylamino ethyl phosphorothionate, isomerization occurs to form the corresponding dialkyl S-ethyl-2-mer-

captoethyl and S-B-diethylaminoethyl phosphorothiolates. McPherson and Johnson (1956) studied the nature of decomposition of parathion, methyl parathion, malathion, and chlorothion. They found that the decomposition of the methyl analogue of parathion occurs in two steps, the first of which generates dimethyl sulfide, sulfur dioxide, and a mixture indicated



to contain mixed poly (aryl metaphosphates). This mixture decomposes, sometimes explosively, to a carbonaceous residue in the second step. Estimated times for decomposition to occur were also given for the 65° to 115°C range.

Many investigations of organophosphorus residues on various plants and crops have been conducted. Reports by researchers indicate that insecticides applied to crops to control destructive insects often remain on or in the plant for extended periods of time. El-Refai and Hopkins (1966) found that parathion deposits had a half-life of one day on bean leaf surfaces and a half-life of 2.4 days for the total plant under controlled environmental conditions. They found parathion degradation products on both glass and leaf surfaces after they were subjected to a light intensity of approximately 800 foot-candles and an ambient temperature of 26-30°C for various time intervals during a ten day period. The decomposition products formed included paraoxon, p nitrophenol and possibly S-ethyl parathion.

Gainsburg et al. (1950) studied parathion under field conditions and found virtually no parathion on crops which were harvested twelve or more days after the last application of dusts or sprays containing 0.125-0.25 lbs per acre. However, they found paraoxon on pea vines which were sprayed with five lbs of parathion per acre nineteen days after application.

Decker et al. (1950) investigating insecticide losses from plants found that the rate of loss of seven insecticides studied occurred in the following order: parathion, lindane, aldrin, chlordane, dieldrin, toxaphen, and DDT. Lindane and parathion were the least persistent of the seven insecticides.

Quinby et al. (1958) reported the half-life of residues of methyl parathion sprayed on cotton leaves was less than one hour under field conditions. The half-life of Guthion spray and dust on cotton leaves appeared to be about two to four days.

Augustinsson and Johnson (1957) found that diazinon when sprayed on Impatiens balsami had a half-life of twenty-five days. After nine weeks the diazinon residue had only twenty percent of the original anti-cholinesterase activity.

Ralls et al. (1966) studied the fate of radioactive diazinon on field grown experimental crops. Diazinon labeled with  $S^{35}$  was sprayed on the agricultural plot and degradation products were studied. The only degradation product identified from the field samples was diazoxon, the oxygen analogue of diazinon.

In summary it can be concluded that the organic phosphorus insecticides are readily converted to anti-ChE inhibitors by exposure to high temperature and light irradiation of various wave lengths. Degradation of organic phosphorus insecticides by photoconversion usually yields the oxygen analogue and the various isomers of the parent compound. Disappearance of insecticide deposits to non-toxic products indicates other pathways also are utilized such as hydrolysis, oxidation, and reduction.

## MATERIALS AND METHODS

### Leaf Surface Residues

#### Rearing of bean plants for growth and green house chamber tests.

Garden bean seeds (Phaseolus vulgaris, bountiful variety) were germinated in vermiculite and nourished at regular intervals with Hyponex nutrient solution (Hydroponic Chemical Co., Inc. Copley, Ohio). After sprouting, the bean plants were transferred to a Hyponex nutrient solution supplemented with iron. The beans were grown under fluorescent and incandescent lights in a laboratory growth chamber (Percival E-57 Environator-Percival Refrigeration and Mfg. Co., Boone, Iowa). The bean plants were exposed to a 16 hour photoperiod (relative humidity was  $40 \pm 5\%$ , temperature  $26^{\circ}\text{C}$ , and a light intensity of 2,500 foot candles) until maximum primary leaf growth was reached in about fifteen days. The bean leaves were then ready for insecticide treatment.

Garden bean seeds of the same variety were germinated in the green house in trays containing a mixture of prepared soil and sand. The bean seeds were irrigated with water daily until sprouting occurred; at that time the seedlings were transferred to individual clay pots. The potted bean plants were irrigated daily while being exposed to the photoperiod of the sun (approx. 16-hours) until maximum primary leaf growth was reached. At that time the bean plants were ready for insecticide treatment and subsequent green house sunlight exposure tests.

Rearing of field foliage. As a part of a large study on insecticide residues, a test plot of irrigated farm land containing approximately twenty acres total area, was subdivided into six regions as illustrated

on PLATE II. Terrace # 1, 2, 3a, 3b, and 4a were planted with field corn (Zea mays, Pioneer 321, .75% Captan treatment). Terrace # 4b was planted with sorghum and was utilized as a control area. The corn and sorghum were exposed to natural field growing conditions supplemented by periodic irrigation to maintain steady plant growth. The field corn was allowed to mature to the stage of development just prior to the "silking" of the corn ear. At that time the corn plants were then ready for insecticide treatment and subsequent residue and degradation investigations.

Application of insecticide to foliage and environmental conditions present in growth chamber, green house, and direct sunlight tests. Bean plants were treated with solutions of insecticide when the primary leaves had reached maximum size. Guthion, diazinon, malathion, parathion and methyl parathion were applied to the upper surfaces of the two primary leaves of each bean plant at 5 mg/leaf. This procedure is illustrated in Fig. 3 of PLATE III. The five organophosphorus insecticides were dissolved in solutions of 95% ethanol and one ml of each insecticide (5 mg/ml) was applied drop-wise from a volumetric pipet and was spread evenly over each leaf with the aid of a camel hair brush in a manner illustrated in Fig. 4 of PLATE III. A slow steady nitrogen air stream aided in the evaporation of the ethanol without injury to the leaf, leaving a deposit of known quantity covering the entire upper leaf surface. Immediately after insecticide application the plants were placed in either the growth chamber or green house for various timed intervals of exposure to light irradiation. The irradiation tests in the growth chamber varied in length from 1 hour of light exposure, (light intensity of 2,500 foot candles, relative humidity  $40 \pm 5\%$ , temperature  $26^{\circ}\text{C}$ ) to 14 days of light exposure under a 16 hour



# PLATE II

(1)	Corn (Diazinon)
(2)	Corn (Not sampled)
(3a)	Corn (Methyl parathion)
(3b)	Corn (Not sampled)
(4b)	Sorghum (Not sampled)
(4a)	Sorghum (Control)



## PLATE III

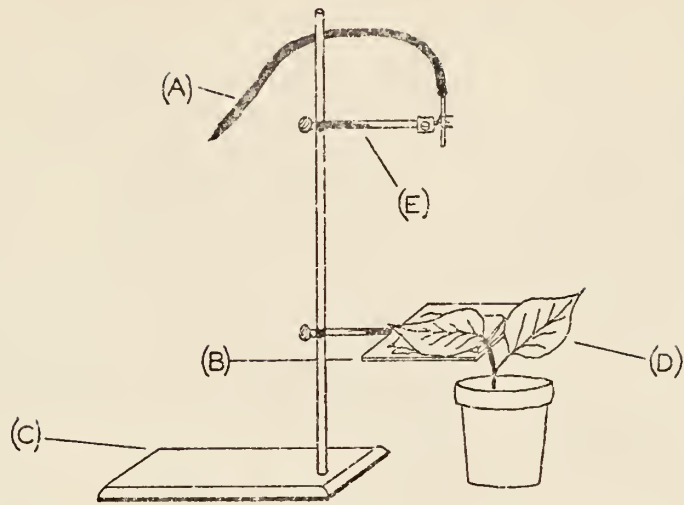


Fig. 3. Insecticide Application Apparatus

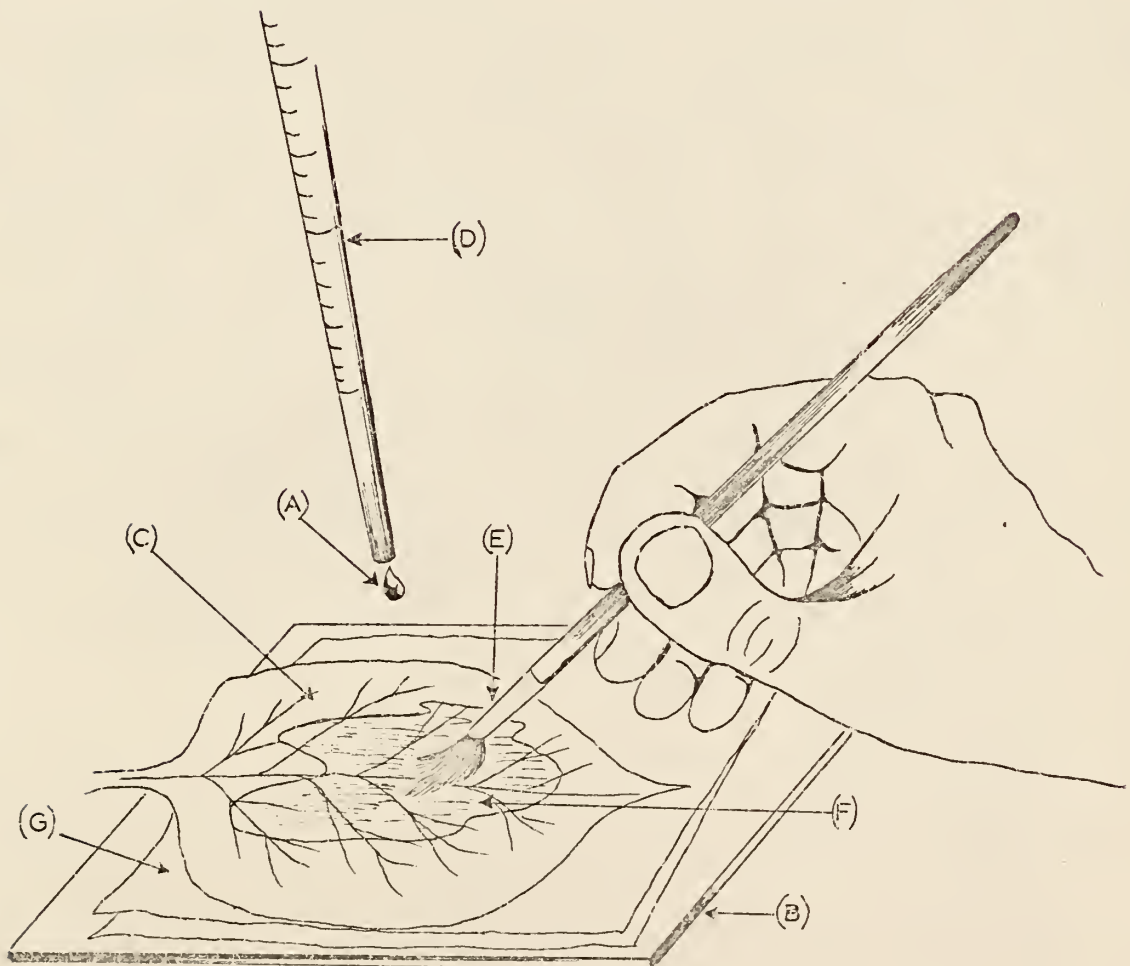


Fig. 4. Application of Insecticide to Leaf Surface

photoperiod per day. The irradiation tests in the green house and in direct sunlight were similar to those conducted in the growth chamber with the exception being a lack of rigid control of the environmental conditions. The bean plants were exposed to direct sunlight and to the sunlight present in the green house, and this light varied in intensity from a low of 10 foot candles to a high reading of 13,400 foot candles. The green house temperature was  $26.7^{\circ}\text{C} \pm 10^{\circ}$ , and the relative humidity was  $50 \pm 20\%$ , and the direct sunlight temperature was  $15-30^{\circ}\text{C}$ , and relative humidity  $50 \pm 10\%$ , 16 hours of light and 8 hours of darkness. The green house bean plants and the direct sunlight plants were exposed to light at the same time intervals as those plants in the growth chamber. The tests ranged in length of exposure from 1 hour to 14 days under green house sunlight conditions, and 1 hour to 96 hours under direct sunlight exposure. A control plant was utilized in the green house and direct sunlight and growth chamber light tests. The control plant was treated with 1 ml of ethanol (95%) and was applied in the same manner as the insecticide ethanol solutions were applied to the treated plants. The control plant was the same variety, age, stage of development, and was subjected to the same growing conditions and light exposure as the insecticide treated bean plants. Glass plates (10 x 10 cm) containing 5 mg/plate were also treated with the five insecticides and exposed along with the bean plants to the various light time intervals.

Application of insecticide to foliage grown under field conditions.

The field test plot containing corn and sorghum (as illustrated in PLATE II) was subjected to aerial insecticide application on August 9,

1967, and samples were taken at various time intervals from terraces # 1, 3a, and 4a.

Collection and removal of insecticide residue from light tests  
conducted in the growth chamber, green house, and direct sunlight. The treated bean leaves exposed to the growth chamber light tests were removed at the time intervals of: 1 hour, 24 hours, 2 days, 5 days, 7 days, and 14 days. Three repetitions of each time interval experiment were performed. The treated foliage in the green house experiments were removed from sunlight exposure after: 1 hour, 2 hours, 6 hours, 12 hours, 1 day, 2 days, 4 days, 5 days, 7 days, and 14 days. The treated foliage in the direct sunlight tests were removed after exposure of: 1, 2, 6, 12, 24, 48, and 96 hours. Three repetitions of the direct sunlight and green house light exposure tests were conducted. The leaf surface insecticide residues resulting from light irradiation in the direct sunlight, green house, and growth chamber were all removed by the same method. The treated leaves were cut at the basal end of the petiole after light exposure at specified time intervals. The cut primary leaf was placed in a glass funnel and the upper leaf surface was washed with 25 ml of redistilled acetone. The acetone wash was collected at the base of the funnel in a collection vial and placed in the freezer (-17.8°C) for later residue analysis.

Collection and removal of insecticide residue from field crops.  
The treated field corn was sampled at time intervals of: 1 hour, 1 day, and repeated at 24 hour intervals until the fourteenth day after application. One final sample was collected on the twenty-first day

after application as a check of the persistence of the applied insecticides. Twenty leaf samples collected each day from each of the treated terraces (terraces # 1, 2, and 3a) and a sample was also collected on the control terrace (# 4b). The samples were collected in a method that can be described as both random and selective. The samples were selective in that only the uppermost leaves, those with the greatest exposure to sunlight and the aerial insecticide application, were selected. The upper leaves were selected at random from the area within each treated terrace. This same procedure of sample collection was used in sampling the control terrace. The foliage samples were cut at the base of the leaf petiole and placed in plastic bags, sealed, and transferred to the laboratory where the insecticide residue was removed by acetone washing of the leaves. The removal of the insecticide residue from the corn leaves was accomplished by washing the upper leaf surface with 50 ml of re-distilled acetone and collecting this leaf wash over a glass funnel and into a collection jar. The acetone leaf residue rinse was transferred from the collection jar to a round-bottom flask containing several boiling chips (glass beads). The residue containing flask was then connected to a Flash Evaporator (Buchler Instruments, Ft. Lee, N. J.). The acetone was removed from the insecticide residue at a temperature of 27°C; which was maintained by a controlled water bath until a final volume of 10 ml was obtained. The leaf residue rinse was removed from the flash evaporator quantitatively and placed in a collection vial and stored at -17.8°C until residue analysis.

Cleanup procedure of foliage insecticide residue. The micromethod of column chromatography sample cleanup reported by Kadoun (1967) was

utilized and slightly modified for the field residue samples. The foliage samples were removed from the freezer and allowed to warm up to room temperature (20-23°C). The leaf extracts were then evaporated to dryness under a stream of nitrogen. The resulting dry extract was redissolved in 1 ml of redistilled n-hexane. One gram of silica gel, 60-200 mesh (Fisher Scientific Company, St. Louis, Mo.) was placed in a disposable pipet which was previously packed with a plug of glass wool about  $1\frac{1}{2}$  in. from the tip of the pipet. The microcolumn was then tapped to obtain good packing and washed with 5 ml of n-hexane. The 1 ml residue extract was saturated with 5  $\mu$ l of distilled water and was transferred to the microcolumn. The extract was allowed to percolate through the column at a rate of 1 ml per 1 to 2 minutes. The walls of the microcolumn were rinsed with small portions of n-hexane. When the solvent reached the top of the silica gel, elution with the desired eluting solvent was commenced. Table 1 lists the selective elution solvent methods to remove insecticides from the column. The eluate was collected from the column until the eluting solvent had reached the upper surface of the silica gel. The eluate obtained was evaporated to dryness by a stream of nitrogen and redissolved in 1 ml of redistilled acetone. This extract was then ready for thin-layer chromatography residue analysis.

#### Glass Surface Residues

##### Preparation and application of insecticides to glass surfaces.

The same insecticide standard solutions (5 mg/ml in 95% ethanol) of diazinon, Guthion, malathion, parathion, and methyl parathion which were applied to the primary bean leaves were used on 10 x 10 cm glass plates.

Table 1. Selective elution of organophosphorus insecticides from micro-column packed with one gram of silica gel.

Insecticide	Solvent system	Total volume of eluate (ml)
Parathion	Benzene	8
Methyl parathion	Benzene	8
Diazinon	8% (v/v) ethyl acetate in benzene	8
Guthion	8% (v/v) ethyl acetate in benzene	8
Malathion	8% (v/v) ethyl acetate in benzene	8

The glass plates were treated with the insecticides using the same method of application as utilized in the bean leaf treatment. One ml of each insecticide was applied drop-wise from a volumetric pipet and was spread evenly over the surface of the glass plate with the aid of a camel hair brush. A slow steady stream of nitrogen aided in the evaporation of the ethanol, leaving a deposit of known quantity covering the upper surface of the glass plate. Immediately after insecticide application the glass plates were placed along with the treated bean leaves in either the growth chamber or the green house for specified time periods of light irradiation.

Exposure procedure of glass plates in the growth chamber and the green house. The treated glass plates were held horizontally at the same height as the treated primary leaves of the bean plants undergoing light irradiation in either the green house or the growth chamber. The

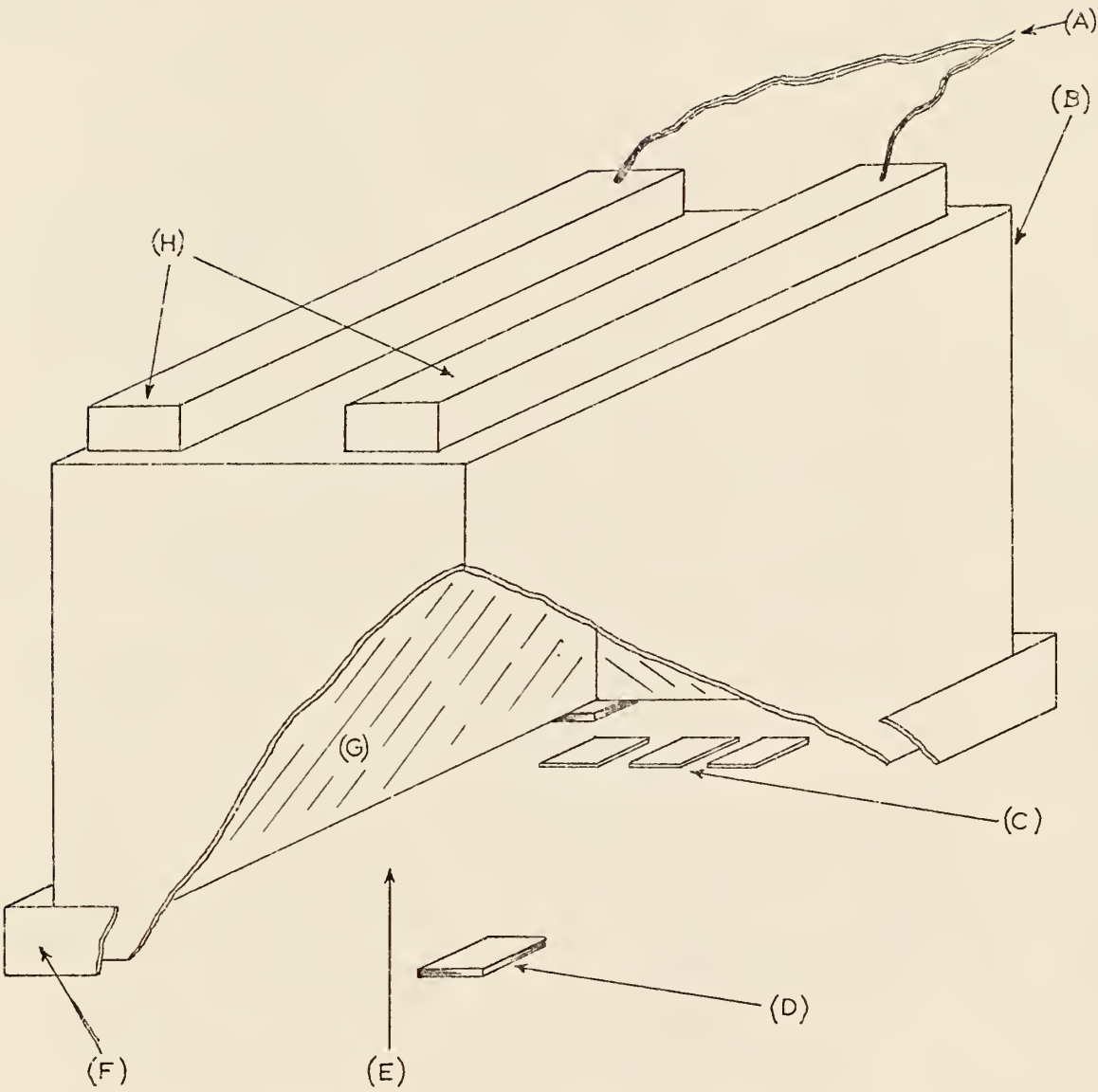
glass plates were subject to the same light intensity, light exposure intervals after insecticide application, and the same growth chamber and green house environmental conditions as previously described. Three replications of light exposure in the growth chamber and green house were performed.

Exposure of glass plates to direct sunlight. Glass plates containing diazinon, malathion, Guthion, methyl parathion, and parathion, were exposed horizontally to direct sunlight. Sunlight intensity varied from 200 foot candles to 13,800 foot candles. The relative humidity was  $30 \pm 10\%$  and the temperature varied from  $16^{\circ}$  to  $30^{\circ}\text{C}$ . The treated glass plates were removed from the sunlight exposure at time intervals of: 1 hour, 2 hours, 3 hours, 6 hours, 12 hours, and 24 hours and immediately were subjected to residue removal and collection.

Light chamber tests. Several light chamber were constructed out of cardboard as illustrated in PLATE IV. The chamber was equipped with two single fluorescent lamp fixtures (Midwest Chandelier Co., Kansas City, Mo.) and was lined on the inside with aluminum foil to aid in light reflection (Koller, 1965). Air was allowed to circulate in the chamber due to the presence of an air vent around the base of the chamber. The light chambers were unchanged for all the tests with the exception of the infrared light test. A modification consisting of a large hole (8 in. diameter) was made in the center of the top of the light chamber; this was to allow the passage of the infrared bulb inside the chamber. Four sources of light irradiation were used in the light chambers to determine the effects of various electromagnetic waves (light) on the



PLATE IV



insecticides of diazinon, Guthion, malathion, methyl parathion, and parathion. The four light sources were: near ultraviolet light lamp, F 15T8-BLB; far ultraviolet light lamp, G 15T8, (both manufactured by General Electric Co., Cleveland, Ohio); plant-GRO lamp, natural sunlight simulation lamp, F1578/GRO (Westinghouse Electric Corp., Bloomfield, N. J.); and a reflector infrared red bowl lamp, R-40, (General Electric Co., Cleveland, Ohio). The relative intensity of each light source as compared with direct sunlight was measured with a photometer. The relative intensities of the light sources are listed in Table 2. The insecticides were exposed to the light sources and also to a control chamber having no light at all, for time intervals of: 1, 3, 6, 12, and 24 hours; 2, 3, 4, 5, 7, and 14 days.

Table 2. Relative intensities of light sources.

Light source	Peak spectrum (Å)	Growth chamber intensity rela- tive to sunlight
Near ultraviolet lamp	3900-4900 <sup>1/</sup>	0.21
Far ultraviolet lamp	2200-2600 <sup>1/</sup>	0.32
Sunlight (avg. day)		1.00
GRO lamp	4300-6400 <sup>2/</sup>	0.32
Infrared lamp	7000-9000 <sup>2/</sup>	0.11
No light		0.00

<sup>1/</sup> Information obtained: General Electric Lamp Division.

<sup>2/</sup> Information source: Westinghouse Lamp Division.

Combination of light sources. Treated glass plates were exposed to two combinations of light sources: the combination of near ultraviolet and far ultraviolet light, and the combination of near ultraviolet light, GRO lamp light, and infrared light. The same five insecticides used in the other light chamber tests were exposed to these two combinations of light sources. The time intervals following application and subsequent removal of the treated glass plates were the same as in the previous light chamber tests as stated in the Materials and Methods. A control chamber having no light irradiation was also utilized in these two experiments.

Collection and removal of insecticides from glass surfaces. Treated glass plates were removed from the source of irradiation after specified time intervals and placed in a glass funnel. The upper surface of the treated glass plate was washed with 10 ml of redistilled acetone and collected at the base of the funnel in a collection vial. The volume of glass plate insecticide residue was evaporated under a stream of nitrogen until a final volume of 1 ml. The 1 ml of residue was stored in a refrigerator until subsequent thin-layer chromatography identification.

### Analytical Procedures

Analytical Standards. Five organophosphorus insecticides containing the thiono sulfur group ( $P=S$ ) were used in the light experiments. Analytical grade standards (99+%) of Guthion, 0,0-dimethyl S-4-oxo-1,2,3-benzotriazin-3 (4H)-ylmethyl phosphorodithioate, obtained from Chemagro Corp., (Kansas City, Missouri); diazinon, 0,0-diethyl 0-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate, obtained from Geigy Chemical

Corp., (Yonkers, New York); parathion, O,O-diethyl O-p-nitrophenyl phosphorothioate, acquired from American Cyanamid Company, (Princeton, N. J.); methyl parathion, O,O-dimethyl O-p-nitrophenyl phosphorothioate, procured from Monsanto Company, (St. Louis, Missouri); and malathion, diethyl mercaptosuccinate, S-ester with O,O-dimethyl phosphorodithioate, obtained from American Cyanamid Corp., (Princeton, N. J.) were prepared in ethanol (95%) solutions at concentrations of 5 mg/ml. The oxygen analogs of the five insecticides were also prepared in the same solvent and concentration. These standards were used in tlc spot identification.

Analytical standards of dimethyl phosphate, potassium O,O, dimethyl phosphorothioate, potassium O,O, dimethyl phosphorodithioate, diethyl phosphorothioate ammonium salt, O,O, diethyl thiophosphoric acid, diethyl phosphorothioic acid, diethyl phosphoric acid, monomethyl phosphate and ortho phosphate were prepared in the same manner and using the same concentrations. These standards were utilized in the spot identification of unknown insecticide breakdown products on paper chromatograms.

Synthesis of methyl paraoxon. Methyl paraoxon could not be obtained from a manufacturer, so the method employed by Berkelhammer et al. (1963) was used in the conversion of methyl parathion to its oxygen analog. A 15 ml diethyl ether solution containing 1.15 gm of methyl parathion (Shell Chemical Co., New York, N. Y.) was placed in a 100 ml, three-hole microwave flask (Metro Industries, N. Y., N. Y.). The flask was fitted with an all glass hollow-bore disposable pipet which was used to introduce dinitrogen tetroxide (Matheson Co., East Rutherford, N. J.) into the methyl parathion ether solution at a steady rate for 30 minutes. The dinitrogen tetroxide passed through two drying towers containing alternate layers of

calcium chloride and Drierite (W. A. Hammon Drierite Co., Xenia, Ohio). During the introduction of the gas, the mixture was stirred with the aid of a magnetic stirrer and a constant temperature (35°C) was maintained. The yellow-brown solution was allowed to stand at the original reaction temperature for 18 hours and a gas was steadily evolved during this time. The solvent was then removed by disconnecting the cylinder of oxidant and drawing a water aspirator produced slow stream of air through the exit drying tube which was placed at the third hole opening in the flask. Solvent stripping time was 30-45 min. The resulting residue was quantitatively transferred to a glass separatory funnel and was washed with 20 ml of redistilled chloroform and then washed with 5 ml of 20% sodium bicarbonate solution. The bicarbonate layer was extracted twice with 5 ml of chloroform and the three chloroform fractions were combined and dried over magnesium sulfate. The resulting oil was removed from the magnesium sulfate and the remaining solvent was removed by passing a stream of nitrogen over the product. A standard ethanol solution containing 5 mg/ml of the product (methyl paraoxon) was prepared and analysed by thin-layer chromatography and infrared spectroscopy.

Preparation of thin-layer plates and paper chromatograms for detection of Phosphorothioate insecticides and their oxygen analogs. Preliminary studies for separation and detection of diazinon, malathion, Guthion, methyl parathion, parathion, their oxygen analogs, and other compounds that might be produced by metabolism or degradation were conducted using thin-layer chromatography. Apparatus, reagents, preparation, washing of adsorbent layers, and storage of prepared plates were according to El-Refai and Hopkins (1965). Chromatography paper strips of Whatman

No. 1 (1 x 8 inches) were washed with acetone:distilled water (1:1 v/v) dried and used for paper chromatography.

Thin-layer and paper chromatography solvent systems. The solvent systems used in thin-layer chromatography were mainly those described by El-Refai and Hopkins (1965). The nonaqueous or normal phase system employed various concentrations of dimethylformamide (Eastman practical grade, Eastman Organic Chemicals, Rochester, N. Y.) as a stationary phase on cellulose and 2,2,4-trimethylpentane (Eastman practical grade) alone or in a mixture with benzene as the mobile phase. The solvent system utilized in paper chromatography was described by Hanes and Isherwood (1949). Ascending paper chromatography solvent systems consisted of several combinations of ammonium hydroxide and isopropanol (25:75% v/v and 15:85% v/v). Another system used consisted of combinations of acetonitrile (practical grade, Fisher Scientific Co.) and distilled water in ratios of: (85:15% v/v), (75:25% v/v), and (60:40% v/v).

Thin-layer and paper chromatography detection reagents. Silver-nitrate-bromophenol blue, (Getz, 1962): The chromatograms were dried at 50°C for 15 minutes and sprayed with the reagent (9 parts of silver nitrate, 1.0% in 75 ml of acetone and 25 ml of water; and 1 part bromophenol blue, 0.4% in acetone) and reheated at 50°C for 10 min. The cooled cellulose plates were carefully immersed in a 0.01% aqueous citric acid until formation of blue spots.

Bromine-fluorescein-silver nitrate: The chromatograms were exposed to bromine vapor for 30 seconds followed by spraying with the fluorescein solution prepared according to Walker and Beroza (1963), then silver nitrate solution. Silver nitrate was prepared according to Mitchell (1960).

Cholinesterase spray: Detection of the anti-ChE active oxygen analogs of the light exposed organophosphorus compounds was according to El-Refai and Hopkins (1965) and Cook (1955). The dried chromatoplates were sprayed with the enzyme-indicator solution from an all glass spray bottle till the cellulose layer was moist, the sprayed chromatoplate was allowed to stand for 20 min. at room temperature, then sprayed with the substrate solution. After 2 min. the areas of inhibition became visible. The visible spots appeared as bright blue spots on a yellow background.

Hanes-Isherwood reagent (1949): The reagent was prepared by adding 2 gm of ammonium molybdate to 10 ml perchloric acid (72-75%) and 1.66 ml concentrated hydrochloric acid and dilution of the solution to a final volume of 200 ml. The reagent was only used on paper chromatograms to detect phosphoric esters of diazinon, malathion, parathion, methyl parathion, and Guthion.

Alcoholic potassium hydroxide: A solution of 5% potassium hydroxide in ethanol (95%) was prepared according to El-Refai and Hopkins (1965) and Metcalf and March (1953). This solution was used to detect parathion, methyl parathion, and their oxons. The sprayed chromatograms were heated to 100°C to give yellow spots on a pale yellow background.

## RESULTS AND DISCUSSION

### Malathion Degradation on Glass and Leaf Surfaces from Light Exposure

Malathion exposure in the growth chamber. The thin-layer chromatographic results of the exposure of malathion in the growth chamber on bean leaves and glass plates are presented in Table 3. Two tlc spots other than the parent compound were found; an unknown (No. 1) and mala-

Table 3. Malathion exposure on bean leaves and glass plates in the growth chamber (26°C, 40 ± 5% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time (days)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Malaoxon	3 Unknown	4 Malathion
1	Leaf	-	-	-	+
	Glass	-	-	-	+
2	Leaf	-	-	-	+
	Glass	-	-	-	+
3	Leaf	-	-	-	+
	Glass	-	+	-	+
5	Leaf	-	+	-	+
	Glass	-	+	-	+
7	Leaf	-	+	-	+
	Glass	+	+	-	+
9	Leaf	+	+	-	+
	Glass	+	+	-	+
12	Leaf	+	+	-	+
	Glass	+	+	-	+
14	Leaf	-	+	-	+
	Glass	-	+	-	+

1/ Numbers correspond to spots in Fig. 5.

oxon. Under growth chamber conditions the malaaxon first appeared on the glass surfaces three days after application. The malaaxon did not appear on the bean leaf surface until the fifth day of growth chamber exposure. The unknown spot detected at the point of origin appeared seven days after application and persisted for five days. The bean leaf and glass plate residues of malathion and malaaxon were detected up to 14 days after application using the tlc system of cellulose plates as explained in Fig. 5. Malathion and malaaxon spots could not be detected at 17 days exposure to growth chamber light.

Malathion exposure in the green house. Thin-layer chromatographic results of the exposure of malathion in the green house are presented in Table 4. Malaaxon and two unknown compounds were detected by the tlc system employed (Fig. 5). The malaaxon first appeared on the glass plate surface 12 hours after exposure to green house light. The malaaxon appeared on the bean leaf surface two days after application. The malaaxon persisted on the glass plates and bean leaves for 14 days in the green house. Malathion was detected throughout the first seven days after application on both glass and bean leaves, but not at 14 days. Unknown compound (No. 3) at  $R_f$  .35 was detected on only the glass plate surfaces at collections of two and four days. The other unknown (No. 1) located at the point of origin was originally thought to be a contaminant but microcolumn cleanup failed to remove the compound. This unknown product first appeared on the leaf surface after 1 day of exposure and on the glass plate surface 2 days after exposure and persisted throughout 14 days.

Table 4. Malathion exposure on bean leaves and glass plates in the green house (16-30°C, 75 ± 10% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 10-13,800 foot candles).

Time	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Malaoxon	3 Unknown	4 Malathion
1 Hour	Leaf	-	-	-	+
	Glass	-	-	-	+
2 "	Leaf	-	-	-	+
	Glass	-	-	-	+
6 "	Leaf	-	-	-	+
	Glass	-	-	-	+
12 "	Leaf	-	-	-	+
	Glass	-	+	-	+
1 Day	Leaf	+	-	-	+
	Glass	-	+	-	+
2 "	Leaf	+	+	-	+
	Glass	+	+	+	+
4 "	Leaf	+	+	-	+
	Glass	+	+	+	+
5 "	Leaf	+	+	-	+
	Glass	+	+	-	+
7 "	Leaf	+	+	-	+
	Glass	+	+	-	+
14 "	Leaf	+	+	-	-
	Glass	+	+	-	-

1/ Numbers correspond to spots in Fig. 5.

Malathion exposure to direct sunlight. The thin-layer chromatographic results of exposure on bean leaves and glass plates of malathion are presented in Table 5. Three breakdown products were detected on glass surfaces and two breakdown products on leaf surfaces. Malaoxon and two unknown products (No. 1 and 3) were found on glass and malaoxon and one unknown product (No. 1) were found on the bean leaves. Malaoxon first appeared on the leaf surface 12 hours after application and on the glass plates 24 hours after application. Unknown product (No. 1) was detected one day after application on both leaf and glass surfaces. This product along with malathion and malaoxon persisted for the entire duration of the exposure interval of 96 hours. The other unknown compound (No. 3) appeared 48 hours after exposure on only the glass surface and was not detected at any other time interval. The direct sunlight tests were terminated after 96 hours due to unfavorable weather conditions.

Malathion exposure on glass plates in the light chamber. Thin-layer chromatographic results of exposure of malathion to near ultraviolet, far ultraviolet, artificial sunlight, infrared, and no light are presented in Table 6. Four spots were detected by thin-layer chromatography of the malathion glass plate residue after exposure to the five previously mentioned light sources as illustrated in Fig. 5. Malathion (No. 4) did not persist longer than two days under near and far ultraviolet, and only one day under infrared. Malathion persisted until the third day in artificial sunlight which was less energetic than the other three light sources. Unknown No. 3 appeared at one day in the infrared and the near and far ultraviolet but was not detected in artificial sunlight until the third day. This unknown at  $R_F$  .35 had a mobility on the chromatogram inter-

Table 5. Malathion exposure on bean leaves and glass plates in the direct sunlight (15-30°C, 50  $\pm$  10% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 10-13,800 foot candles).

Time (hours)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <sup>1/</sup>			
		1 Unknown	2 Malaoxon	3 Unknown	4 Malathion
1	Leaf	-	-	-	+
	Glass	-	-	-	+
2	Leaf	-	-	-	+
	Glass	-	-	-	+
6	Leaf	-	-	-	+
	Glass	-	-	-	+
12	Leaf	-	+	-	+
	Glass	-	-	-	+
24	Leaf	+	+	-	+
	Glass	+	+	-	+
48	Leaf	+	+	-	+
	Glass	+	+	+	+
96	Leaf	+	+	-	+
	Glass	+	+	-	+

<sup>1/</sup> Numbers correspond to spots in Fig. 5.

Table 6. Malathion exposure on glass plates in the light chamber (26°C,  $40 \pm 5\%$  r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <sup>2/</sup>	Time (days)	Spots as indicated by tlc <sup>1/</sup>			
		1 Unknown	2 Malaoxon	3 Unknown	4 Malathion
A	1	-	+	+	+
	2	+	+	+	+
	3	+	+	+	-
	4	+	+	+	-
	5	+	+	+	-
	7	+	+	-	-
	14	+	-	-	-
B	1	+	+	+	+
	2	+	+	+	+
	3	+	+	+	-
	4	+	+	+	-
	5	+	+	-	-
	7	+	+	-	-
	14	+	-	-	-
C	1	-	-	-	+
	2	-	+	-	+
	3	+	+	+	+
	4	+	+	+	-
	5	+	+	+	-
	7	+	-	-	-
	14	+	-	-	-
D	1	-	+	+	+
	2	+	-	-	-
	3	+	-	-	-
	4	-	-	-	-
	5	-	-	-	-
	7	-	-	-	-
	14	-	-	-	-
E	1	-	-	-	+
	2	-	-	-	+
	3	-	-	-	+
	4	-	-	-	+
	5	-	-	-	+
	7	-	-	-	+
	14	-	+	-	+

<sup>1/</sup> Numbers correspond to spots in Fig. 5.

<sup>2/</sup> Light sources: A Near ultraviolet light  
 B Far ultraviolet light  
 C Artificial sunlight  
 D Infrared light  
 E Control or absence of all light

mediate between malathion and malaaxon indicating it could possibly be the S-methyl isomer of malathion. Malaaxon (No. 2) appeared at one day then disappeared from the plates subjected to infrared. Under the near and far ultraviolet the malaaxon persisted from the first through the seventh day. Malaaxon persisted under artificial sunlight from the third to the fifth day. It was observed that malaaxon did not persist for more than two days after the disappearance of malathion indicating malaaxon was constantly being formed from malathion and the spot detected did not actually indicate persistence but rather indicated the presence of malaaxon. Unknown(s) (No. 1) which could possibly be the mono and or dicarboxylic acid derivatives of malathion appeared early in the near and far ultraviolet and indicated a degree of stability by persisting until termination of the experiment. This unknown(s) was present at three days in the artificial sunlight and was detected until the end of the experiment. The infrared experiment did not exhibit a tlc spot for this unknown after the third day of exposure indicating decomposition or volatilization from the surface due to heat. The control exhibited only one noticeable change and that was the presence of malaaxon in the 14 day sample, which indicates malathion can be converted to its oxon in absence of light by the presence of atmospheric oxygen.

Paper chromatographic results of malathion exposure to the five light sources are presented in Table 7. The paper chromatograms were developed using Hanes-Isherwood spray reagent (see Fig. 6) and six hydrolytic breakdown products were found to be present.

Dimethyl phosphorodithioate (No. 6), dimethyl phosphorothioate (No. 5), dimethyl phosphate (No. 4), and monomethyl phosphate (No. 2) were readily

Table 7. Malathion exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <u>2/</u>	Time (days)	Spots as indicated by paper chromatography <u>1/</u>					
		1	2	3	4	5	6
A	1	+	+	-	+	+	+
	2	+	+	-	+	+	+
	3	+	+	-	+	+	+
	4	+	+	-	+	+	+
	5	+	-	-	-	-	-
	7	+	-	-	-	-	-
	14	+	-	-	-	-	-
B	1	+	+	+	+	+	+
	2	+	+	-	+	+	+
	3	+	+	-	+	+	+
	4	+	+	-	+	+	+
	5	+	-	-	-	-	-
	7	+	-	-	-	-	-
	14	+	-	-	-	-	-
C	1	-	-	-	-	-	-
	2	+	+	-	+	+	+
	3	+	+	+	+	+	+
	4	+	+	-	+	+	+
	5	+	-	-	+	+	-
	7	+	-	-	+	+	-
	14	+	-	-	-	-	-
D	1	+	+	+	+	+	+
	2	+	-	-	+	-	-
	3	+	-	-	-	-	-
	4	+	-	-	-	-	-
	5	+	-	-	-	-	-
	7	+	-	-	-	-	-
	14	+	-	-	-	-	-
E	1	-	-	-	-	-	-
	2	-	-	-	-	-	-
	3	-	-	-	-	-	-
	4	-	-	-	-	-	-
	5	-	-	-	-	-	-
	7	-	-	-	-	-	-
	14	-	-	-	-	-	-

1/

1. Ortho phosphate
2. Monomethyl phosphate
3. Unknown
4. Dimethyl phosphate
5. Dimethyl phosphorothioate
6. Dimethyl phosphorodithioate

2/

- A Near ultraviolet light
- B Far ultraviolet light
- C Artificial sunlight
- D Infrared radiation
- E Control or no light

Numbers correspond to spots in Fig. 6.

Experimental

Standards

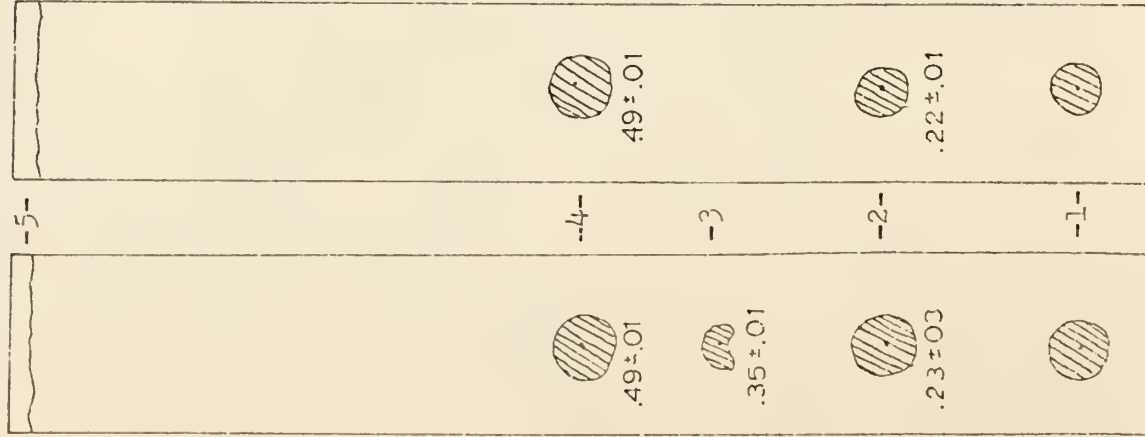


Fig. 5

Fig. 5. Thin layer chromatography of malathion breakdown products on leaves and glass plates after exposure to sunlight, artificial sunlight, near and far ultraviolet, and infrared

TLC plates coated with cellulose; immobile phase, 15% dimethylformamide in acetone; mobile phase 15% benzene in isooctane; development, bromophenol blue reagent

1. Solvent origin (degradation products)
  2. Malaoxon
  3. Unknown
  4. Malathion
  5. Solvent front
- Mean R<sub>f</sub> and standard deviation

Experimental

Standards

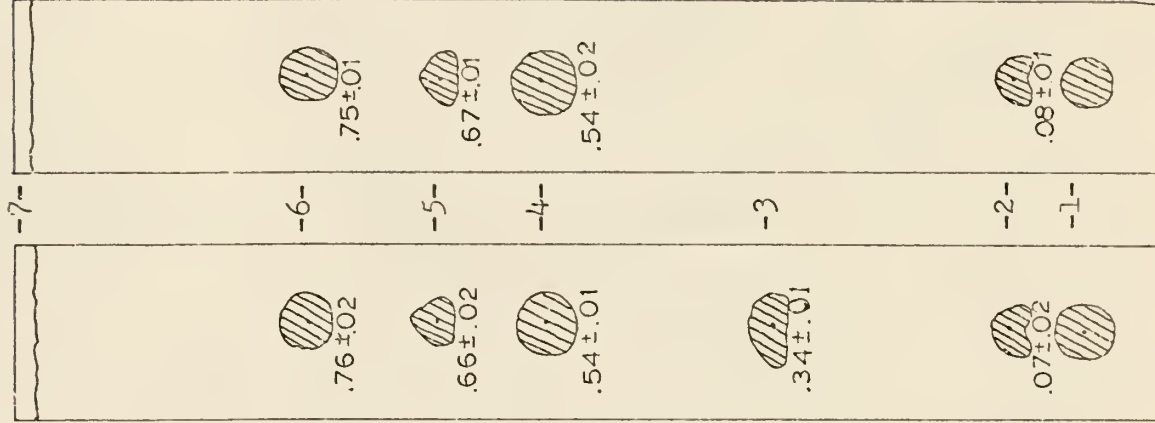


Fig. 6

Fig. 6. Paper chromatography of malathion breakdown products on glass plates after exposure to sunlight, artificial sunlight, near and far ultraviolet, and infrared.

Paper chromatograms were Whatman No. 1 strips; immobile phase, none; mobile phase, 25% NH<sub>4</sub>OH in iso-propanol; development, Kanes-Isherwood reagent.

1. Ortho phosphate
2. Monomethyl phosphate
3. Unknown
4. Dimethyl phosphate
5. Dimethyl phosphorothioate
6. Dimethyl phosphorodithioate
7. Solvent front

formed under near and far ultraviolet on the first day and persisted through the fourth day. Ortho phosphate which is relatively stable was present from the first to the 14 day under both ultraviolet sources. The same products were formed under the artificial sunlight but did not appear until the second day of exposure due to the lower energy of the light source. Infrared exposure caused all hydrolytic products to be formed on the first day but accelerated their disappearance with the exception of ortho phosphate. An unknown (No. 3) was found in the infrared, far ultraviolet and artificial sunlight but could not be identified by comparison with known standards. No hydrolytic products were formed in the control environment further emphasizing the importance of light in the degradation of malathion.

Malathion degradation products and possible breakdown routes. A possible degradation scheme of events indicating how the compounds identified by thin-layer and paper chromatography could be formed is illustrated in Fig. 7.

It was observed in the removal of malathion from the glass plates that the insecticide was not spread as a continuous film, but rather was in the form of small droplets that were evenly distributed over the surface. This condition was not present or noticed at the time of application, and was probably caused by the evaporation of the solvent. The color of the malathion residues depended on the type of light exposure the glass plate had been subjected to. Generally, the more active the light source such as infrared or far ultraviolet, and or the longer the period of exposure, the darker the malathion residue became. The color range of the residue was from clear to pale yellow to dark brown.



The relative energy of the light sources was reflected in the time required for the tlc detection of malaaxon and the unknown(s) (No. 1). Malaaxon was detected on the third day in the growth chamber, at two days in artificial sunlight, at one day in the infrared, near and far ultraviolet and at 12 hours in the green house and direct sunlight. The green house light and the direct sunlight, which were essentially the same, converted malathion to its oxon rapidly due to greater light intensity. Apparently the ultraviolet and infrared regions are most effective in catalyzing the oxidation of malathion in the presence of atmospheric oxygen and this would be expected to hold true for sunlight. The unknown(s) (No. 1) detected at the point of origin could have been the mono or dicarboxylic acid derivatives of malathion since these are more polar metabolites than malaaxon and would be expected to remain near the origin of the chromatograms. The detecting spray reagent (see Fig. 6) indicates that unknown(s) (No. 1) is a sulfur containing phosphate ester which is further evidence for these derivatives. Unknown (No. 3) at  $R_f$  .35 would correspond to the area where one might expect the S-methyl isomer of malathion to be present since this compound is intermediate in polarity between malathion and malaaxon. This unknown spot also had anticholinesterase activity which is further evidence for the S-methyl isomer.

A number of hydrolytic degradation products of malathion, malaaxon and their corresponding mono and di acid derivatives were detected on the paper chromatograms. The sequence of events shows a progressive shift from the less polar dimethyl phosphoric acid analogs to more acidic mono and ortho phosphates. The higher energy light sources again

caused these products to appear more rapidly. The relative activity or energy availability of the light sources tested, based upon number of breakdown products found in the least amount of time required are: direct sunlight, green house light, infrared, far ultraviolet, near ultraviolet, artificial sunlight, growth chamber light, and no light.

#### Guthion Degradation on Glass and Leaf Surfaces after Light Exposure

Guthion exposure in the growth chamber. The thin-layer chromatographic results of Guthion in the growth chamber on bean leaves and glass plates are presented in Table 8. Two tlc spots other than the parent compound were found: an unknown(s) (No. 1) and Gutoxon (No. 2), as illustrated in Fig. 8. Under growth chamber conditions the Gutoxon appeared on the glass and leaf surfaces on the fifth day of exposure and persisted until the 14 day. The unknown appeared nine days after application on the glass and leaves and was detected for five days. Guthion, Gutoxon and the unknown could not be detected at 17 days exposure to growth chamber light.

Guthion exposure in the green house. Thin-layer chromatographic results of the exposure of Guthion in the green house are presented in Table 9. Gutoxon (No. 2) first appeared on the bean leaf surface 12 hours after exposure and on the glass plates 24 hours after exposure. Gutoxon and Guthion (No. 4) persisted on the glass and bean leaf surface for 14 days, but neither compound could be detected at 17 days. Unknown(s) (No. 1) was detected at the origin on the glass and bean leaf surfaces at the same time intervals as Gutoxon, and persisted until

Table 8. Guthion exposure on bean leaves and glass plates in the growth chamber ( $26^{\circ}\text{C}$ ,  $40 \pm 5\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time (days)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Gutaxon	3 Unknown	4 Guthion
1	Leaf	-	-	-	+
	Glass	-	-	-	+
2	Leaf	-	-	-	+
	Glass	-	-	-	+
3	Leaf	-	-	-	+
	Glass	-	-	-	+
5	Leaf	-	+	-	+
	Glass	-	+	-	÷
7	Leaf	-	+	-	+
	Glass	-	+	-	+
9	Leaf	+	+	-	+
	Glass	+	+	-	+
12	Leaf	+	+	-	+
	Glass	+	+	-	+
14	Leaf	+	+	-	+
	Glass	+	+	-	+

1/ Numbers correspond to spots in Fig. 8.

Table 9. Guthion exposure on bean leaves and glass plates in the green house (16-30°C, 75  $\pm$  20% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Gutoxon	3 Unknown	4 Guthion
1 Hour	Leaf	-	-	-	+
	Glass	-	-	-	+
2 "	Leaf	-	-	-	+
	Glass	-	-	-	+
6 "	Leaf	-	-	-	+
	Glass	-	-	-	+
12 "	Leaf	+	+	-	+
	Glass	-	-	-	+
24 "	Leaf	+	+	-	+
	Glass	+	+	-	+
2 Days	Leaf	+	+	-	+
	Glass	+	+	+	+
4 "	Leaf	+	+	-	+
	Glass	+	+	-	+
5 "	Leaf	+	+	-	+
	Glass	+	+	-	+
7 "	Leaf	+	+	-	+
	Glass	+	+	-	+
14 "	Leaf	+	+	-	+
	Glass	+	+	-	+

1/ Numbers correspond to spots in Fig. 8.

the 14 day. This unknown which would represent more extensive degradation than Gutoxon because of its highly polar nature occurred at a much earlier interval than in the growth chamber because of the higher energy and intensity of sunlight. An unknown (No. 3) was detected only in the two day glass plate sample. This unknown which is more polar than Guthion but less polar than Gutoxon, would be in the range of the S-methyl isomer of Guthion.

Guthion exposure to direct sunlight. The thin-layer chromatographic results of Guthion exposure on glass and leaf surfaces are presented in Table 10. Three breakdown products were detected on the glass surfaces and two breakdown products on the leaf surfaces as illustrated in Fig. 8. Gutoxon and the two products were found on glass; Gutoxon and product (No. 1) were found on bean leaf surfaces. Gutoxon appeared on glass and leaf surfaces after 12 hours and persisted for the entire duration of the exposure interval of 96 hours. Unknown (No. 1) first appeared on the glass plate surface after 24 hours and on the bean leaf surface 48 hours after application, and was more polar than Gutoxon. Compound (No. 3) was found only on glass at 24 hours. It was observed that this compound, which was previously mentioned as the S-methyl isomer of Guthion, was found in the green house and direct sunlight only on the glass surfaces and had a very limited persistence. The reason this compound was not detected on the bean leaf surface may be due to the chemical nature of the leaf which could either hinder its formation or absorb it into the leaf. Guthion was detected every time interval sampled in the direct sunlight test.

Table 10. Guthion exposure on bean leaves and glass plates in the direct sunlight (15-30°C, 50  $\pm$  10% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 10-13,800 foot candles).

Time (hours)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Gutoxon	3 Unknown	4 Guthion
1	Leaf	-	-	-	+
	Glass	-	-	-	+
2	Leaf	-	-	-	+
	Glass	-	-	-	+
6	Leaf	-	-	-	+
	Glass	-	-	-	+
12	Leaf	-	+	-	+
	Glass	-	+	-	+
24	Leaf	-	+	-	+
	Glass	+	+	+	+
48	Leaf	+	+	-	+
	Glass	+	+	-	+
96	Leaf	+	+	-	+
	Glass	+	+	-	+

1/ Numbers correspond to spots in Fig. 8.

Guthion exposure on glass plates in the light chamber. Thin-layer chromatographic results of exposure of Guthion to the five previously mentioned light sources are presented in Table 11. Four spots were detected by thin-layer chromatography as illustrated in Fig. 8. Guthion (No. 4) persistence was the greatest under the artificial sunlight test followed by: near ultraviolet, far ultraviolet and infrared. Compound (No. 3), possibly S-methyl isomer of Guthion, was detected first under the heat of the infrared and this would be expected since isomerization is particularly liable to occur on heating of the phosphorodithioates. This compound was detected under the light sources in the following order: infrared, far ultraviolet, near ultraviolet and artificial sunlight. The persistence under each light source was for a period of three days. Gutoxon was readily detected under the infrared and far ultraviolet at one day and appeared at two days under near ultraviolet and artificial sunlight. Unknown (No. 1) was found in all the time interval samples of near and far ultraviolet and was absent only in the 14 day sampling of the infrared exposure. This spot at the point of origin appeared at the fourth day and persisted for 10 days under artificial sunlight. The Guthion control exhibited only one noticeable change and that was the presence of Gutoxon in the 14 day sample, indicating that the parent compound in the absence of light can be oxidized in the presence of atmospheric oxygen.

Paper chromatographic results of guthion exposure to the five light sources are presented in Table 12. The paper chromatograms were developed using the Hanes-Isherwood spray reagent (Fig. 9) and seven breakdown products were detected. Ortho phosphate, monomethyl phosphate,

Table 11. Guthion exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <u>2/</u>	Time (days)	Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Gutoxon	3 Unknown	4 Guthion
A	1	+	-	-	+
	2	+	+	-	+
	3	+	+	+	+
	4	+	+	+	+
	5	+	+	+	+
	7	+	-	-	-
	14	+	-	-	-
B	1	+	+	-	+
	2	+	+	+	+
	3	+	+	+	+
	4	+	+	+	+
	5	+	-	-	-
	7	+	-	-	-
	14	+	-	-	-
C	1	-	-	-	+
	2	-	+	-	+
	3	-	+	-	+
	4	+	+	+	+
	5	+	+	+	+
	7	+	+	+	+
	14	+	-	-	-
D	1	+	+	+	+
	2	+	+	+	+
	3	+	+	+	+
	4	+	-	-	-
	5	+	-	-	-
	7	+	-	-	-
	14	-	-	-	-
E	1	-	-	-	+
	2	-	-	-	+
	3	-	-	-	+
	4	-	-	-	+
	5	-	-	-	+
	7	-	-	-	+
	14	-	+	-	-

1/ Numbers correspond to spots in Fig. 8.

2/ Light sources: A Near ultraviolet light  
 B Far ultraviolet light  
 C Artificial sunlight  
 D Infrared light  
 E Control or absence of all light.

Table 12. Guthion exposure on glass plates in the light chamber (26°C, 40  $\pm$  5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <sup>2/</sup>	Time (days)	Spots as indicated by paper chromatography <sup>1/</sup>						
		1	2	3	4	5	6	7
A	1	-	-	-	-	-	-	-
	2	+	+	-	-	-	+	-
	3	+	+	+	-	+	+	+
	4	+	+	+	-	+	+	+
	5	+	-	-	+	-	+	+
	7	+	-	-	-	-	-	+
	14	+	-	-	-	-	-	-
B	1	+	-	-	-	-	+	-
	2	+	+	-	-	+	+	-
	3	+	+	+	-	+	+	+
	4	+	+	+	-	+	+	+
	5	+	-	-	+	-	+	+
	7	+	-	-	-	-	-	+
	14	+	-	-	-	-	-	-
C	1	-	-	-	-	-	-	-
	2	-	-	-	-	-	-	-
	3	-	-	-	-	-	-	+
	4	+	+	-	-	+	-	+
	5	+	+	+	+	+	+	+
	7	+	-	-	+	-	-	+
	14	+	-	-	-	-	-	-
D	1	+	-	-	-	-	+	-
	2	+	+	-	-	-	+	-
	3	+	+	+	-	+	+	+
	4	+	+	+	-	+	+	+
	5	+	-	-	-	-	+	+
	7	+	-	-	-	-	-	+
	14	+	-	-	-	-	-	-
E	1	-	-	-	-	-	-	-
	2	-	-	-	-	-	-	-
	3	-	-	-	-	-	-	-
	4	-	-	-	-	-	-	-
	5	-	-	-	-	-	-	-
	7	-	-	-	-	-	-	-
	14	-	-	-	-	-	-	-

- <sup>1/</sup> 1. Ortho phosphate  
 2. Monomethyl phosphate  
 3. Unknown  
 4. Unknown  
 5. Dimethyl phosphate  
 6. Dimethyl phosphorothioate  
 7. Dimethyl phosphorodithioate

- <sup>2/</sup> A Near ultraviolet light  
 B Far ultraviolet light  
 C Artificial sunlight  
 D Infrared radiation  
 E Control or no light

Numbers correspond to spots in fig. 9

Experimental

Standards

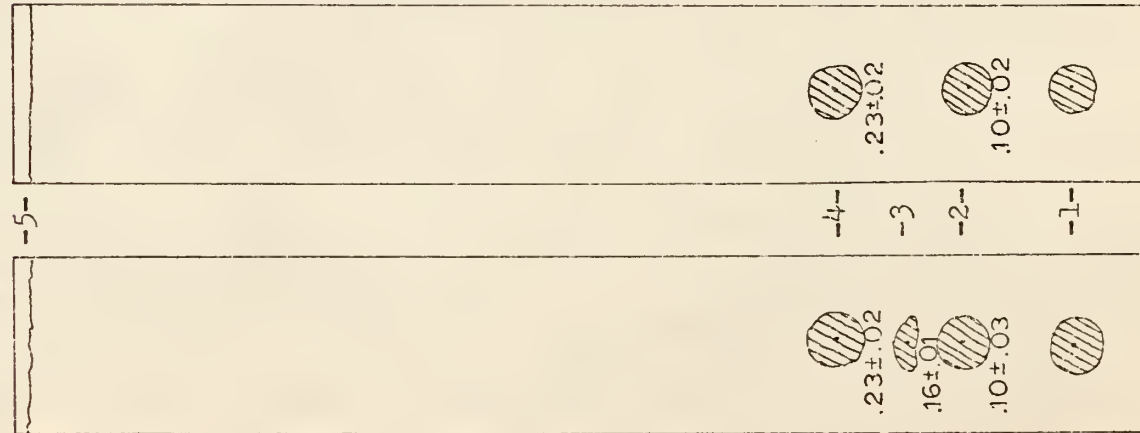


Fig. 8. Thin layer chromatography of Guthion and breakdown products on leaves and glass plates after exposure to sunlight, artificial sunlight, near and far ultraviolet, and infrared.

The tlc plates were coated with cellulose; immobile phase, 20% dimethylformamide in acetone; mobile phase, 25% benzene in isooctane; development, bromophenol blue reagent.

1. Solvent origin (degradation products)

2. Gutoxon

3. Unknown product

4. Guthion

5. Solvent front

Mean R<sub>f</sub> value and standard deviation.

Experimental

Standards

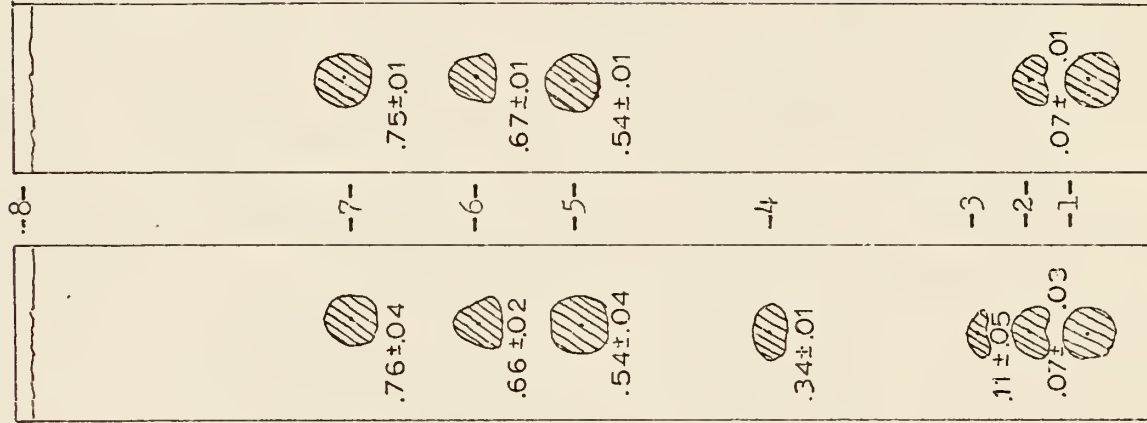


Fig. 9. Paper chromatography of Guthion and breakdown products on glass plates after exposure to sunlight, artificial sunlight, near and far ultraviolet, and infrared.

Paper chromatograms were Whatman No. 1 strips; immobile phase, none; mobile phase, 25% NH<sub>4</sub>OH in iso-propanol; development, Manes-Isherwood reagent.

1. Ortho phosphate

2. Monomethyl phosphate

3. Unknown

4. Unknown

5. Dimethyl phosphate

6. Dimethyl phosphorothioate

7. Dimethyl phosphorodithioate

8. Solvent front

Fig. 8

Fig. 9

dimethyl phosphate, dimethyl phosphorothioate, dimethyl phosphorodithioate and two unknown compounds were identified as breakdown products of Guthion by comparison with known standards. It was observed that the paper chromatographic results of the far and near ultraviolet tests were almost identical, the only difference being, the presence of dimethyl phosphorothioate (No. 6) at one day in the far ultraviolet and at two days in the near ultraviolet, and (No. 5) was detected one day later in the near ultraviolet. Both light sources indicated the presence of an unknown (No. 4) compound at five days. This compound had an intermediate polarity between dimethyl phosphate and monomethyl phosphate. Unknown (No. 3) was also detected under both light sources at  $R_f$  .11. Since the reagent used in detection was Hanes-Isherwood the two unknown compounds would be phosphoric esters. The only product detected at 14 days and present at 14 days in all four light sources was ortho phosphate indicating this compound may be the eventual stable degradation end product of Guthion. The comparison of paper chromatographic results of artificial sunlight with infrared generally indicated the presence of the same compounds only at different time intervals and lengths of persistence. The infrared indicated the phosphoric esters of Guthion at an earlier time than under artificial sunlight. There were two noticeable differences between the infrared and artificial sunlight tests. (1) Unknown (No. 4) was present at five and seven days in the artificial sunlight but was not found at all under infrared. This could be interpreted to mean that this compound is not stable under infrared or the infrared does not catalyze the formation of this compound. (2) The presence of dimethyl phosphorothioate was indicated for five days under infrared (and four and five days under

near and far ultraviolet) but was only present at the fifth day under artificial sunlight. The four light sources indicated the presence of dimethyl phosphorothioate at five days but not at seven days. The more energetic light sources seem to speed up the formation of compound (No. 6). The comparison of the five light sources indicated the infrared and far ultraviolet to be the most active followed by the near ultraviolet, artificial sunlight and no light. The control or no light exposure exhibited no spots when sprayed with the Hanes-Isherwood reagent.

Guthion degradation products and possible breakdown routes. In the removal of Guthion from the glass plates it was observed that the insecticide was not spread as a continuous film, but rather existed in the same form of small droplets as did the malathion. The color of the Guthion glass plate residue rinses ranged from clear-pale yellow-dark yellow. The color of the residue depended upon the type and duration of light exposure. The energy levels of the light sources were reflected in the time required for the detection of Gutoxon and the unknown(s) (No. 1). Gutoxon was detected on the fifth day in the growth chamber, at two days under artificial sunlight and near ultraviolet, at one day in the infrared and far ultraviolet and at 12 hours in the green house and direct sunlight. Unknown No. 1 was detected at nine days in the growth chamber, at four days under artificial sunlight, at one day in the near and far ultraviolet, infrared, direct sunlight, and green house. Unknown No. 3 as was previously mentioned was thought to be the S-methyl isomer of Guthion.

The paper chromatographic results support or indicate the same general energetic activity levels of the light sources as were found in

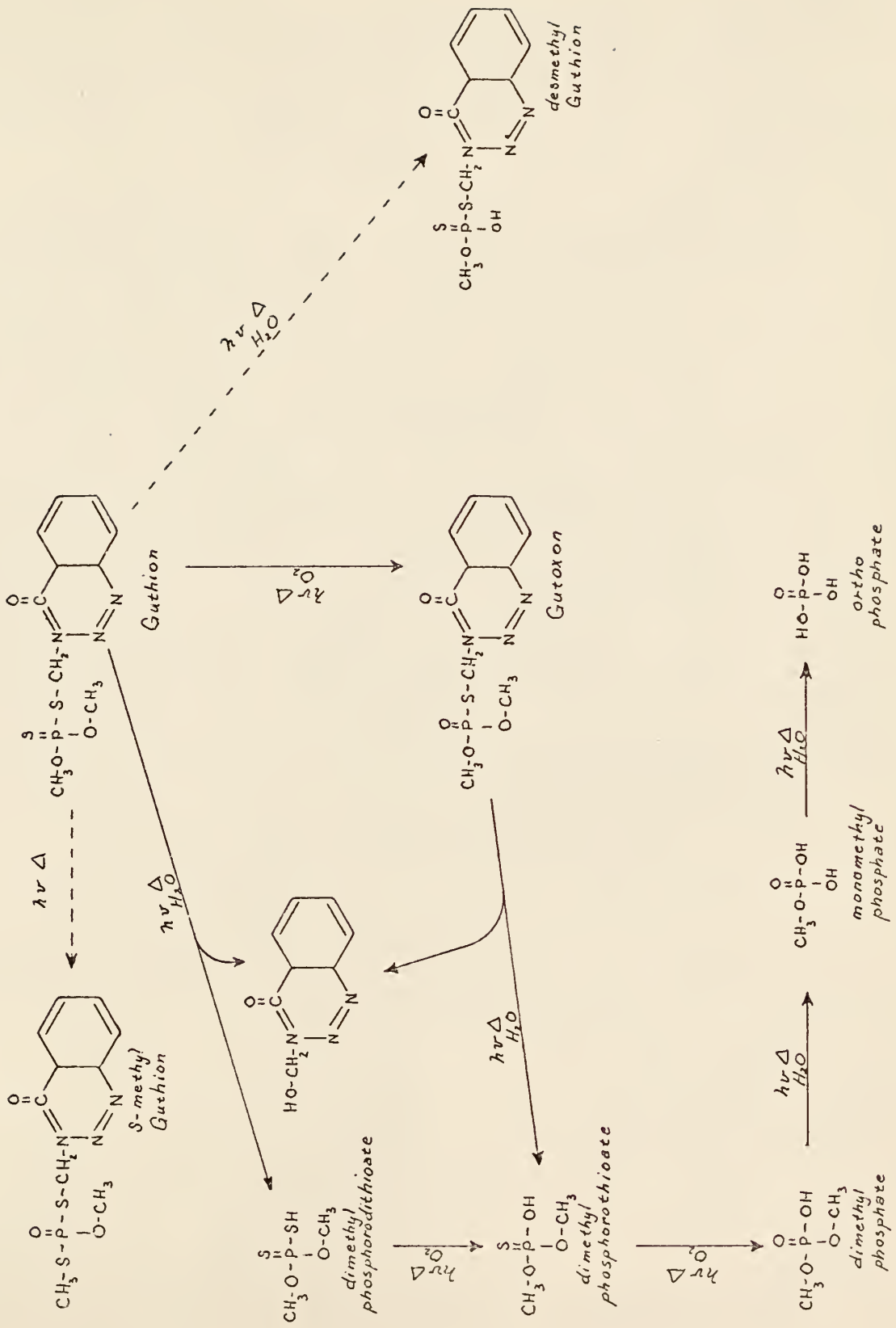


Fig. 10

the thin-layer chromatographic results. The relative activity or energy availability of the light sources tested, based upon number of breakdown products indicated in the least amount of time are: direct sunlight, green house light, infrared, far ultraviolet, near ultraviolet, artificial sunlight, growth chamber light, and no light. A possible degradation scheme of events indicating how the thin-layer and paper chromatographic identified compounds could be formed is illustrated in Fig. 10.

#### Methyl Parathion Degradation on Glass and Leaf Surfaces from Light Exposure

Methyl parathion exposure in the growth chamber. The thin-layer chromatographic results of the exposure of methyl parathion in the growth chamber on bean leaves and glass plates are presented in Table 13. Five tlc spots other than the parent compound were detected; three unknown compounds (No. 1, 5, and 6), p-nitrophenol (No. 2) and methyl paraoxon (No. 3) as illustrated in Fig. 11. Under growth chamber conditions methyl paraoxon was the first breakdown product detected on the bean leaves and glass plates. The oxon was detected at three days on the leaf surface and at five days on the glass surface. The next two compounds which were detected were p-nitrophenol and unknown (No. 1); they were detected on both surfaces at seven days and persisted until termination of the experiment. Unknowns (No. 5 and 6) could possibly be the S-phenyl and S-methyl isomer of parathion because they were less polar than methyl paraoxon but more polar than the parent compound and gave a positive reaction when sprayed with the cholinesterase spray reagent. The tlc spots were detected in the area where one would expect to find the isomers of methyl parathion. These two unknowns were detected

Table 13. Methyl parathion exposure on bean leaves and glass plates in the growth chamber (26°C, 40 ± 5% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time (days)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)						
		Spots as indicated by tlc <sup>1/</sup>						
		1	2	3	4	5	6	7 <sup>2/</sup>
1	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
2	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
3	Leaf	-	-	+	-	-	-	+
	Glass	-	-	-	-	-	-	+
5	Leaf	-	-	+	-	-	-	+
	Glass	-	-	+	-	-	-	+
7	Leaf	+	+	+	-	-	-	+
	Glass	+	+	+	-	-	-	+
9	Leaf	+	+	+	-	-	-	+
	Glass	+	+	+	-	+	-	+
12	Leaf	+	+	+	-	-	-	+
	Glass	+	+	+	-	+	+	+
14	Leaf	+	+	+	-	-	-	+
	Glass	+	+	+	-	-	-	+

<sup>1/</sup> Numbers correspond to spots in fig. 11

- <sup>2/</sup>
1. Unknown
  2. p-nitrophenol
  3. Methyl paraoxon
  4. Unknown
  5. Unknown
  6. Unknown
  7. Methyl parathion

only on the glass plate surface. The detection spray reagent of alcoholic KOH indicated the four unknown spots of methyl parathion contained the *p*-nitrophenol moiety. The parent compound was present in every sample taken but could not be detected at 17 days. A control experiment of treated bean leaves and glass plates in a no light enclosure indicated the presence of methyl paraoxon after 14 days on both surfaces, but no other degradation product was found. The control containing untreated bean leaves and glass plates in the growth chamber did not produce any spots which corresponded to the breakdown products detected on the treated bean leaves and glass plates.

Methyl parathion exposure in the green house. The thin-layer chromatographic results of methyl parathion exposure in the green house are presented in Table 14. Methyl paraoxon first appeared on the leaf surface at 12 hours and on the glass surface at 24 hours and persisted until termination of the experiment. The *p*-nitrophenol was the second compound to be detected on the leaf and glass surface. This compound was detected at 24 hours on the leaf surface and at two days on the glass surface and until the seventh day after application. Unknown No. 5 was first detected at 4 days on the bean leaves and 24 hours later was detected on the glass plates. The compound persisted on both surfaces for two days. The other unknown (No. 6) was found on both surfaces at five days but was only detected on the glass plates at seven days. The parent compound persisted under green house conditions until the seventh day. The unknown(s) (No. 1) was first detected at four days on the leaf surface and at five days on the glass surface; this compound was detected at 14 days. The results obtained in the green house and growth chamber

Table 14. Methyl parathion exposure on bean leaves and glass plates in the green house ( $16-30^{\circ}\text{C}$ ,  $75 \pm 20\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)						
		Spots as indicated by tlc <u>1/</u>						
		1	2	3	4	5	6	7 <u>2/</u>
1 hours	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
2 "	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
6 "	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
12 "	Leaf	-	-	+	-	-	-	+
	Glass	-	-	-	-	-	-	+
24 "	Leaf	-	+	+	-	-	-	+
	Glass	-	-	+	-	-	-	+
2 days	Leaf	-	+	+	-	-	-	+
	Glass	-	+	+	-	-	-	+
4 "	Leaf	+	+	+	-	+	-	+
	Glass	-	+	+	-	-	-	+
5 "	Leaf	+	+	+	-	+	+	+
	Glass	+	+	+	-	+	+	+
7 "	Leaf	+	+	+	-	-	-	+
	Glass	+	+	+	-	+	+	+
14 "	Leaf	+	-	+	-	-	-	-
	Glass	+	-	+	-	-	-	-

1/ Numbers correspond to spots in fig. 11

- 2/
1. Unknown
  2. p-nitrophenol
  3. Methyl paraoxon
  4. Unknown
  5. Unknown
  6. Unknown
  7. Methyl parathion

show that methyl parathion is degraded to compounds which are more polar than the parent compound.

Methyl parathion exposure to direct sunlight. Thin-layer chromatographic results of methyl parathion exposure on glass and leaf surfaces are presented in Table 15. Methyl paraoxon was found on glass and bean leaves at 12 hours and persisted until termination of the experiment. Glass plates first indicated the presence of the compound(s) (No. 1) and also the unknown (No. 5). These same compounds were not detected on the leaf surfaces until one day later, but both compounds were detected at the termination of the experiment. The compound thought to be the S-methyl isomer or S-phenyl isomer was detected first on glass at 48 hours and persisted on both surfaces at 96 hours. Unknown (No. 1) which contained the *p*-nitrophenol moiety was present at the termination of the experiment. A direct sunlight control experiment consisting of untreated leaves and glass plates produced spots by the tlc methods employed; but they did not have comparable  $R_f$  values of any methyl parathion breakdown product detected.

Methyl parathion exposure on field corn plants in the direct sunlight. Thin-layer chromatographic results of methyl parathion exposure on field corn in direct sunlight are presented in Table 16. Under direct sunlight methyl parathion persisted until the ninth day. Unknown (No. 6) possibly a methyl parathion isomer was present on the sixth and seventh day of exposure. The other unknown which could possibly be the S-methyl or S-phenyl isomer of methyl parathion was present for four days and was first detected on the fifth day. One compound which was found in the

Table 15. Methyl parathion exposure on bean leaves and glass plates in the direct sunlight ( $15-30^{\circ}\text{C}$ ,  $50 \pm 10\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 10-13,800 foot candles).

Time (hours)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)						
		Spots as indicated by tlc <u>1/</u>						
		1	2	3	4	5	6	7 <u>2/</u>
1	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
2	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
6	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
12	Leaf	-	-	+	-	-	-	+
	Glass	-	-	+	-	-	-	+
24	Leaf	-	-	+	-	-	-	+
	Glass	+	-	+	-	+	-	+
48	Leaf	+	+	+	-	+	-	+
	Glass	+	+	+	-	+	+	+
96	Leaf	+	+	+	-	+	+	+
	Glass	+	+	+	-	+	+	+

1/ Numbers correspond to spots in fig. 11

- 2/
1. Unknown
  2. p-nitrophenol
  3. Methyl paraoxon
  4. Unknown
  5. Unknown
  6. Unknown
  7. Methyl parathion

light chamber tests (No. 4) was not found on the corn plant leaves in the field test. The oxygen analog of methyl parathion was the first breakdown product which was detected on the corn leaves. This observation coincided with the results in the green house, direct sunlight and growth chamber. Methyl paraoxon was present on the corn leaves from the first to the tenth day under field conditions. This oxon was detected for only one day after the disappearance of the parent compound. The detection of another breakdown compound, p-nitrophenol was indicated at two days and persisted until the eighth day. Unknown (No. 1) which was detected long after the disappearance of the other breakdown products, appeared to be a stable intermediate or end product of the degradation of methyl parathion.

Methyl parathion exposure on glass plates in the light chamber. The thin-layer chromatographic results of methyl parathion exposure to five light sources are presented in Table 17. Seven spots were detected by thin-layer chromatography as illustrated in Fig. 11. Methyl parathion persistence was the greatest under artificial sunlight, followed by: near ultraviolet, far ultraviolet and infrared. Unknowns (No. 5 and 6) which were thought to be the S-phenyl and S-methyl isomers of the parent compound, were detected at equal lengths of time under artificial sunlight and near and far ultraviolet. These two compounds showed the least amount of persistence under the infrared. They were detected first under the infrared, then under the far and near ultraviolet and last under the artificial sunlight. Unknown (No. 4) was first detected under infrared, then under far ultraviolet, near ultraviolet and artificial sunlight.

Table 16. Aerial application of methyl parathion on corn plants in direct sunlight (13-31°C, 50  $\pm$  20% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 5-14,200 foot candles).

Time (days)	Presence of compounds indicated by (+) and absence indicated by (-)						
	Spots as indicated by tlc <u>1/</u>						
	1	2	3	4	5	6	7 <u>2/</u>
0	-	-	-	-	-	-	+
1	-	-	+	-	-	-	+
2	-	+	+	-	-	-	+
3	-	+	+	-	-	-	+
4	-	+	+	-	-	-	+
5	-	+	+	-	+	-	+
6	+	+	+	-	+	+	+
7	+	+	+	-	+	+	+
8	+	+	+	-	+	-	+
9	+	-	+	-	-	-	+
10	+	-	+	-	-	-	-
11	+	-	-	-	-	-	-
12	+	-	-	-	-	-	-
13	+	-	-	-	-	-	-
14	+	-	-	-	-	-	-
18	+	-	-	-	-	-	-

1/ Numbers correspond to spots in fig. 11

- 2/
1. Unknown
  2. p-nitrophenol
  3. Methyl paraoxon
  4. Unknown
  5. Unknown
  6. Unknown
  7. Methyl parathion

Table 17. Methyl parathion exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <u>2/</u>	Time (days)	Spots as indicated by tlc <u>1/</u>						
		1	2	3	4	5	6	7
A	1	-	+	+	-	-	-	+
	2	+	+	+	-	-	-	+
	3	+	+	+	-	+	+	+
	4	+	+	+	+	+	+	+
	5	+	+	+	-	+	+	+
	7	+	+	+	-	-	-	-
	14	+	-	-	-	-	-	-
B	1	+	+	+	-	-	-	+
	2	+	+	+	-	+	+	+
	3	+	+	+	+	+	+	+
	4	+	+	+	-	+	+	-
	5	+	+	+	-	-	-	-
	7	+	-	-	-	-	-	-
	14	+	-	-	-	-	-	-
C	1	-	-	+	-	-	-	+
	2	-	+	+	-	-	-	+
	3	-	+	+	-	-	-	+
	4	+	+	+	-	+	+	+
	5	+	+	+	-	+	+	+
	7	+	+	+	+	+	+	+
	14	+	-	-	-	-	-	-
D	1	+	+	+	+	+	+	+
	2	+	+	+	-	+	+	-
	3	+	+	+	-	-	-	-
	4	+	-	-	-	-	-	-
	5	+	-	-	-	-	-	-
	7	+	-	-	-	-	-	-
	14	-	-	-	-	-	-	-
E	1	-	-	-	-	-	-	+
	2	-	-	-	-	-	-	+
	3	-	-	-	-	-	-	+
	4	-	-	-	-	-	-	+
	5	-	-	-	-	-	-	+
	7	-	-	-	-	-	-	+
	14	-	-	+	-	-	-	+

1/

1. Unknown
2. p-nitrophenol
3. Methyl paraoxon
4. Unknown
5. Unknown
6. Unknown
7. Methyl parathion

2/

- A Near ultraviolet
- B Far ultraviolet
- C Artificial sunlight
- D Infrared
- E Control or absence of all light

This compound was detected at only one day of duration under all four light sources. Methyl paraoxon indicated the least amount of persistence under the infrared followed by: far ultraviolet, near ultraviolet and artificial sunlight. All four light sources indicated the presence of this oxon at one day of exposure. The p-nitrophenol was detected at the identical time intervals with the methyl paraoxon under the infrared, far ultraviolet, and near ultraviolet. This same compound was detected from the second to the seventh day under artificial sunlight; this persistence almost coincided with methyl paraoxon persistence. Unknown (No. 1) persisted longer than any other breakdown product under the infrared, indicating this compound was fairly stable under the thermal irradiation of the infrared. This unknown was the last product detected under the four light sources and this suggested the compound may very well be the stable end product of the photodegradation of methyl parathion but further evidence is needed before a conclusion can be reached.

Paper chromatography results of methyl parathion exposure to the five light sources are presented in Table 18. The paper chromatograms were developed as previously described in the results (see Fig. 12). Five breakdown products were detected: ortho phosphate, monomethyl phosphate, dimethyl phosphate, dimethyl phosphorothioate and one unknown compound. The far and near ultraviolet indicated the greatest persistence of dimethyl phosphorothioate; it was detected from the second through seventh days under both ultraviolet light conditions. This same compound was detected at the fourth day and persisted until the seventh day under artificial sunlight. The infrared was the only light source to indicate the presence of dimethyl phosphorothioate at one day. Com-

Table 18. Methyl parathion exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <sup>2/</sup>	Time (days)	Spots as indicated by paper chromatography <sup>1/</sup>				
		1	2	3	4	5
A	1	-	-	-	-	-
	2	+	+	+	-	+
	3	+	+	-	+	+
	4	+	+	-	+	+
	5	+	+	-	+	+
	7	+	+	-	+	+
	14	+	-	-	-	-
B	1	-	-	-	-	-
	2	+	+	-	+	+
	3	+	+	-	+	+
	4	+	+	-	+	+
	5	+	+	-	+	+
	7	+	+	-	+	+
	14	+	-	-	-	-
C	1	-	-	-	-	-
	2	-	-	-	-	-
	3	-	-	-	-	-
	4	+	+	-	+	+
	5	+	+	-	+	+
	7	+	+	-	+	+
	14	+	-	-	-	-
D	1	+	+	+	+	+
	2	+	-	-	+	-
	3	+	-	-	-	-
	4	+	-	-	-	-
	5	+	-	-	-	-
	7	+	-	-	-	-
	14	-	-	-	-	-
E	1	-	-	-	-	-
	2	-	-	-	-	-
	3	-	-	-	-	-
	4	-	-	-	-	-
	5	-	-	-	-	-
	7	-	-	-	-	-
	14	-	-	-	-	-

- <sup>1/</sup>
1. Orthophosphate
  2. Monomethyl phosphate
  3. Unknown
  4. Dimethyl phosphate
  5. Dimethyl phosphorothioate
  6. Solvent front

- <sup>2/</sup>
- A Near ultraviolet
  - B Far ultraviolet
  - C Artificial sunlight
  - D Infrared
  - E Control or absence of all light

Numbers correspond to spots in Fig. 12

## Experimental

## Standards

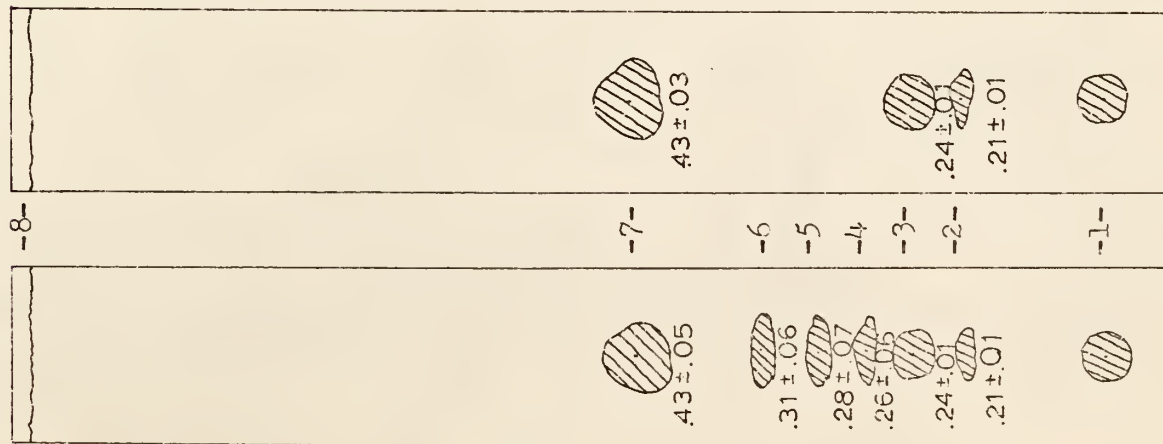


Fig. 11. Thin layer chromatography of methyl parathion and breakdown products on leaves and glass plates after exposure to sunlight, artificial sunlight, near and far ultraviolet, and infrared.

The tlc plates were coated with cellulose; immobile phase, 20% dimethylformamide in acetone; mobile phase, isooctane; development, 5% KOH in 95% ethanol reagent.

1. Solvent origin
2. p-nitrophenol
3. Methyl paraoxon
4. Unknown
5. Unknown
6. Unknown
7. Methyl parathion
8. Solvent front

Mean  $R_f$  value and standard deviation.

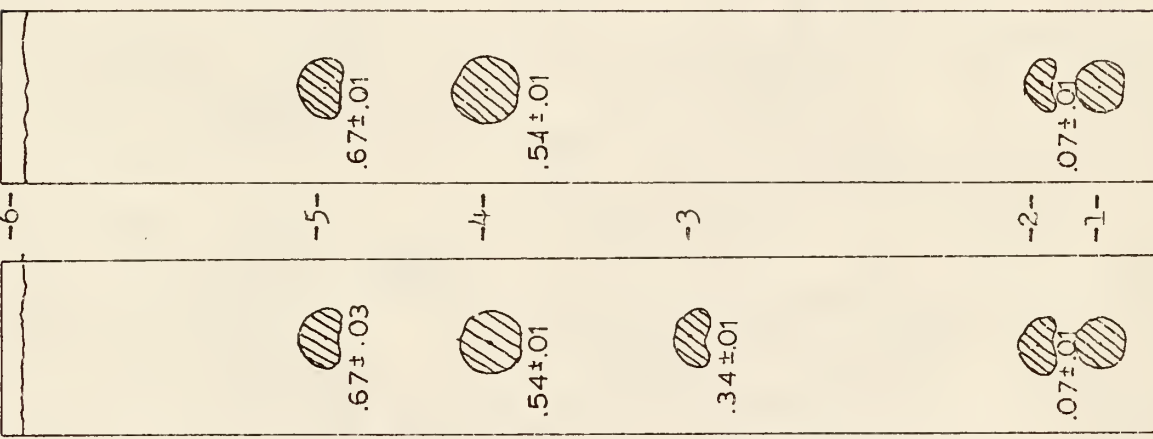


Fig. 12. Paper chromatography of methyl parathion and breakdown products on glass plates after exposure to sunlight, artificial sunlight, near and far ultraviolet and infrared.

Paper chromatograms were Whatman No. 1 strips; mobile phase, 25%  $\text{NH}_4\text{OH}$  in iso-propyl alcohol; development, Hanes-Isherwood reagent.

1. Ortho phosphate
2. Monomethyl phosphate
3. Unknown
4. Dimethyl phosphate
5. Dimethyl phosphorothioate
6. Solvent front

Fig. 11

Fig. 12

pound (No. 4) dimethyl phosphate, indicated the greatest persistence under the far and near ultraviolet followed by: artificial sunlight and infrared. Unknown (No. 3) was detected at the second day under the near ultraviolet and at the first day of infrared exposure. This compound was not detected under any other light source or at any other time interval. Monomethyl phosphate (No. 2) was detected only at the first day of infrared exposure and from the fourth through seventh days under artificial sunlight. This compound was detected at identical time periods in both of the ultraviolet light sources, from the second to the seventh day. The ortho phosphate was present from the second to the 14 day under the two ultraviolet light sources and from the fourth until experiment termination under the artificial sunlight. It was observed that infrared exposure indicated the presence of this compound at the first day but it did not readily disappear as did the other phosphoric acid esters, it remained until the seventh day. These results are similar to the findings which were exhibited by the other two dimethyl phosphorus containing insecticides which were examined.

#### Methyl parathion degradation products and possible breakdown routes.

A probable degradation scheme indicating the routes the thin-layer and paper chromatographic identified compounds could have followed is presented in Fig. 13.

The results obtained in the light exposure tests indicated the first breakdown product was methyl paraoxon, the photooxidation product of the parent compound. The next breakdown products which appear have an intermediate polarity between methyl parathion and its oxon which would correspond to the isomers or p-amino analogs. The paper chromatographic results indicate the hydrolysis of the parent compound occurs

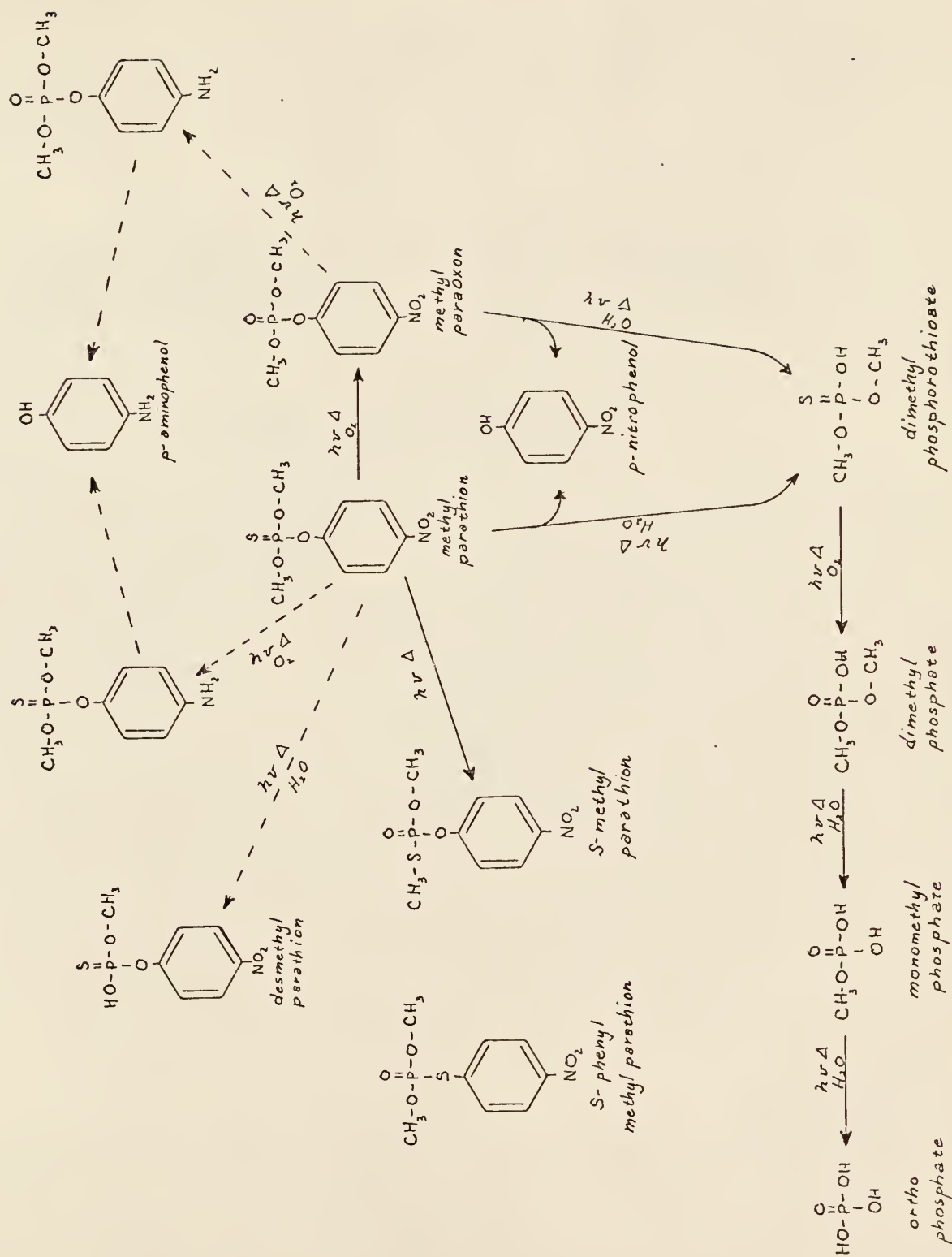


Fig. 13

quite readily with the formation of hydrolytic products which increase in polarity with each successive degradation step. The energy levels of the light sources were reflected in the time required for the detection of the first breakdown product which was methyl paraoxon. The first breakdown product was detected under growth chamber light on the third day, on the first day under artificial sunlight, near ultraviolet, far ultraviolet, infrared, and under direct sunlight in field growing conditions, at 12 hours in the green house and under direct sunlight exposure. Paper chromatographic results of methyl parathion support the thin-layer findings in relation to the general energetic activity levels of the four individual light sources tested. The relative activity or energy availability of the light sources tested based upon number of breakdown products in the least amount of time are: infrared, near and far ultraviolet, direct sunlight, green house irradiation, field study light, artificial sunlight, growth chamber light and no light.

#### Diazinon Degradation on Glass and Leaf Surfaces from Light Exposure

Diazinon exposure in the growth chamber. The thin-layer chromatographic results of diazinon in the growth chamber on bean leaves and glass plates are presented in Table 19. Two tlc spots other than the parent compound were found; an unknown(s) (No. 1) and diazoxon (No. 2) as illustrated in Fig. 14. Under growth chamber conditions the diazoxon first appeared on the bean leaf surface at five days and on the glass plate surface at seven days and persisted on both surfaces until termination of the experiment. The parent compound, diazinon, was detected until the 12 day after application. Unknown(s) (No. 1) was present from

Table 19. Diazinon exposure on bean leaves and glass plates in the growth chamber ( $26^{\circ}\text{C}$ ,  $40 \pm 5\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time (days)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Unknown	3 Diazoxon	4 Diazinon
1	Leaf	-	-	-	+
	Glass	-	-	-	+
2	Leaf	-	-	-	+
	Glass	-	-	-	+
3	Leaf	-	-	-	+
	Glass	-	-	-	+
5	Leaf	-	-	+	+
	Glass	-	-	-	+
7	Leaf	-	-	+	+
	Glass	-	-	+	+
9	Leaf	+	-	+	+
	Glass	+	-	+	+
12	Leaf	+	-	+	+
	Glass	+	-	+	+
14	Leaf	+	-	+	-
	Glass	+	-	+	-

1/ Numbers correspond to spots in Fig. 14.

the ninth to the termination of the experiment and was thought to be hydrolysis degradation products of diazinon.

Diazinon exposure in the green house. Thin-layer chromatographic results of the exposure of diazinon in the green house are listed in Table 20. Diazinon (No. 4) was present at every time interval through seven days, but was not present at 14 days. Diazoxon (No. 3) was the first degradation product of diazinon to make its appearance and was first found at two days. The oxon of diazinon persisted as long as diazinon was present, indicating a constant formation and dissipation. The spot intensity detected remained constant throughout the experiment until the disappearance of the parent compound. Unknown (No. 2) was detected on the glass and leaf samples at four days through seven days but was not detected at 14 days. This unknown at  $R_f .10$ , which was more polar than diazoxon, corresponded in polarity and  $R_f$  value with a known standard of 2-isopropyl-4-methyl-pyrimidin-6-ol (primidinol derivative). The primidinol derivative at  $R_f .10 \pm .1$  could be a likely hydrolysis product of diazinon as illustrated in the diazinon degradation scheme in Fig. 16. The other unknown (No. 1) was first detected on the leaf surface at four days, and on the glass surface 24 hours later. This compound(s) persisted until termination of the green house irradiation experiment.

Diazinon exposure to direct sunlight. The thin-layer chromatographic results of diazinon exposure on glass and leaf surfaces are presented in Table 21. Three breakdown products were detected on the glass and leaf surfaces. Diazoxon was the first product detected and appeared on glass 24 hours after application. Diazoxon was present at 48 hours on both

Table 20. Diazinon exposure on bean leaves and glass plates in the green house ( $16-30^{\circ}\text{C}$ ,  $75 \pm 20\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <sup>1/</sup>			
		1 Unknown	2 Unknown	3 Diazoxon	4 Diazinon
1 hour	Leaf	-	-	-	+
	Glass	-	-	-	+
2 "	Leaf	-	-	-	+
	Glass	-	-	-	+
6 "	Leaf	-	-	-	+
	Glass	-	-	-	+
12 "	Leaf	-	-	-	+
	Glass	-	-	-	+
24 "	Leaf	-	-	-	+
	Glass	-	-	-	+
2 Days	Leaf	-	-	+	+
	Glass	-	-	+	+
4 "	Leaf	+	+	+	+
	Glass	-	+	+	+
5 "	Leaf	+	+	+	+
	Glass	+	+	+	+
7 "	Leaf	+	+	+	+
	Glass	+	+	+	+
14 "	Leaf	+	-	-	-
	Glass	+	-	-	-

<sup>1/</sup> Numbers correspond to spots in Fig. 14.

Table 21. Diazinon exposure on bean leaves and glass plates in the direct sunlight ( $15-30^{\circ}\text{C}$ ,  $50 \pm 10\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 10-13,800 foot candles).

Time (hours)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)			
		Spots as indicated by tlc <u>1/</u>			
		1 Unknown	2 Unknown	3 Diazoxon	4 Diazinon
1	Leaf	-	-	-	+
	Glass	-	-	-	+
2	Leaf	-	-	-	+
	Glass	-	-	-	+
6	Leaf	-	-	-	+
	Glass	-	-	-	+
12	Leaf	-	-	-	+
	Glass	-	-	-	+
24	Leaf	-	-	-	+
	Glass	-	-	+	+
48	Leaf	-	+	+	+
	Glass	-	-	+	+
96	Leaf	+	+	+	+
	Glass	+	+	+	+

1/

Numbers correspond to spots in Fig. 14.

surfaces and persisted until unfavorable weather forced a termination of the experiment at 96 hours (4 days). Unknown (No. 2) which as previously mentioned was thought to be the primidinol derivative of diazinon was first found on the bean leaf surface at 48 hours and was detected on the glass surface at 96 hours. The other unknown which as previously mentioned was thought to be a hydrolysis product(s) was detected only at 96 hours after application. Diazinon was detected at every time interval sampled in the direct sunlight test.

Diazinon exposure on field corn in direct sunlight. Thin-layer chromatographic results of diazinon exposure on a test plot of corn are presented in Table 22. Diazinon was present on the corn until the seventh day after application. Diazoxon appeared two days after aerial application and persisted until 2 days after the disappearance of the parent compound. Unknown No. 2, possibly the primidinol derivative, was detected at two days and persisted until the ninth day which was the same day the diazoxon failed to indicate its presence. The unknown at the origin was first detected at four days and was present in the final sample taken at 18 days. Observations indicate this unknown product(s) to be a stable intermediate or end product of the degradation of diazinon.

Diazinon exposure on glass plates in the light chamber. Thin-layer chromatographic results of diazinon exposure to five light sources are presented in Table 23. Four spots were detected by thin-layer chromatography as illustrated in Fig. 14. Diazinon (No. 4) persistence was the greatest under artificial sunlight, followed by: near ultraviolet, far ultraviolet, and infrared. Diazoxon was easily formed under the near,

Table 22. Aerial application of diazinon on corn plants in direct sunlight (13-31°C, 50 ± 20% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 5-14,200 foot candles).

Time (days)	Presence of compounds indicated by (+) and absence indicated by (-)			
	Spots as indicated by tlc <sup>1/</sup>			
	1 Unknown	2 Unknown	3 Diazoxon	4 Diazinon
0	-	-	-	+
1	-	-	-	+
2	-	+	+	+
3	-	+	+	+
4	+	+	+	+
5	+	+	+	+
6	+	+	+	+
7	+	+	+	+
8	+	+	+	-
9	+	+	+	-
10	+	-	-	-
11	+	-	-	-
12	+	-	-	-
13	+	-	-	-
14	+	-	-	-
18	+	-	-	-

<sup>1/</sup> Numbers correspond to spots in Fig. 14.

Table 23. Diazinon exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <sup>2/</sup>	Time	Spots as indicated by tlc <sup>1/</sup>			
		1 Unknown	2 Unknown	3 Diazoxon	4 Diazinon
A	3 Hours	-	-	+	+
	12 "	-	-	+	+
	24 "	+	+	+	+
	3 Days	+	+	+	+
	5 "	+	-	-	-
	7 "	+	-	-	-
	14 "	+	-	-	-
B	3 Hours	-	-	+	+
	12 "	+	+	+	+
	24 "	+	+	+	+
	3 Days	+	-	+	-
	5 "	+	-	-	-
	7 "	+	-	-	-
	14 "	+	-	-	-
C	3 Hours	-	-	-	+
	12 "	-	-	-	+
	24 "	-	-	-	+
	3 Days	-	-	+	+
	5 "	+	+	+	+
	7 "	+	-	+	-
	14 "	+	-	-	-
D	3 Hours	+	+	+	+
	12 "	+	+	+	-
	24 "	-	-	-	-
	3 Days	-	-	-	-
	5 "	-	-	-	-
	7 "	-	-	-	-
	14 "	-	-	-	-
E	3 Hours	-	-	-	+
	12 "	-	-	-	+
	24 "	-	-	-	+
	3 Days	-	-	-	+
	5 "	-	-	-	+
	7 "	-	-	-	+
	14 "	-	-	+	+

<sup>1/</sup> Numbers correspond to spots in Fig. 14.

<sup>2/</sup> A Near ultraviolet  
 B Far ultraviolet  
 C Artificial sunlight  
 D Infrared  
 E Control or absence of all light

far ultraviolet and infrared and persisted until the third day under both ultraviolet exposures, but was not present after 12 hours under infrared irradiation. Diazoxon was detected first at three days under artificial sunlight. Unknown (No. 2) was present in the thermal active infrared of the photon emitting ultraviolet sources at earlier time periods than in the artificial sunlight. The other unknown at the point of origin was always the last compound to be detected. This was additional evidence that the unknown(s) (No. 1) represented a stable breakdown product of diazinon. The tlc diazinon results of the four light sources indicate that the infrared was the most active light source followed by: far ultraviolet, near ultraviolet, and artificial sunlight. The diazinon control which was in a chamber having no light did not exhibit any noticeable change when examined by thin-layer chromatography.

Paper chromatographic results of diazinon exposure to the five light sources are presented in Table 24. The paper chromatograms were developed as previously described in the results (see Fig. 15). Four breakdown products of diazinon were detected: ortho phosphate, diethyl phosphate, diethyl phosphorothioate, and an unknown, possibly monoethyl phosphate. It was observed that the paper chromatographic results of the two ultraviolet exposures were almost the same. The only differences detected were the presence of diethyl phosphorothioate at three hours in the far ultraviolet while it was not detected until six hours in the near ultraviolet, and ortho phosphate persisted longer under the near ultraviolet. Diethyl phosphorothioate was the first detectable spot in all four light sources; and was detected at three and six hours under infrared and only persisted at three days under artificial sunlight. Diethyl phosphate

Table 24. Diazinon exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <u>2/</u>	Time	Spots as indicated by paper chromatography <u>1/</u>			
		1	2	3	4
A	3 Hours	-	-	-	-
	6 "	+	-	-	+
	12 "	+	+	+	+
	24 "	+	-	+	+
	3 Days	+	-	-	-
	7 "	-	-	-	-
	14 "	-	-	-	-
B	3 Hours	-	-	-	+
	6 "	+	-	-	+
	12 "	+	+	+	+
	24 "	+	-	+	-
	3 Days	-	-	-	-
	7 "	-	-	-	-
	14 "	-	-	-	-
C	3 Hours	-	-	-	-
	6 "	-	-	-	-
	12 "	-	-	-	-
	24 "	-	-	-	-
	3 Days	+	-	+	+
	7 "	+	-	+	-
	14 "	+	-	-	-
D	3 Hours	+	+	+	+
	6 "	+	+	+	+
	12 "	+	-	+	-
	24 "	+	-	-	-
	3 Days	-	-	-	-
	7 "	-	-	-	-
	14 "	-	-	-	-
E	3 Hours	-	-	-	-
	6 "	-	-	-	-
	12 "	-	-	-	-
	24 "	-	-	-	-
	3 Days	-	-	-	-
	7 "	-	-	-	-
	14 "	-	-	-	-

1/ Numbers correspond to spots in Fig. 15.

1. Ortho phosphate
2. Monoethyl phosphate
3. Diethyl phosphoric acid
4. Diethylthio phosphoric acid

2/

- A Near ultraviolet
- B Far ultraviolet
- C Artificial sun-light
- D Infrared
- E Control or absence of all light

Fig. 14.

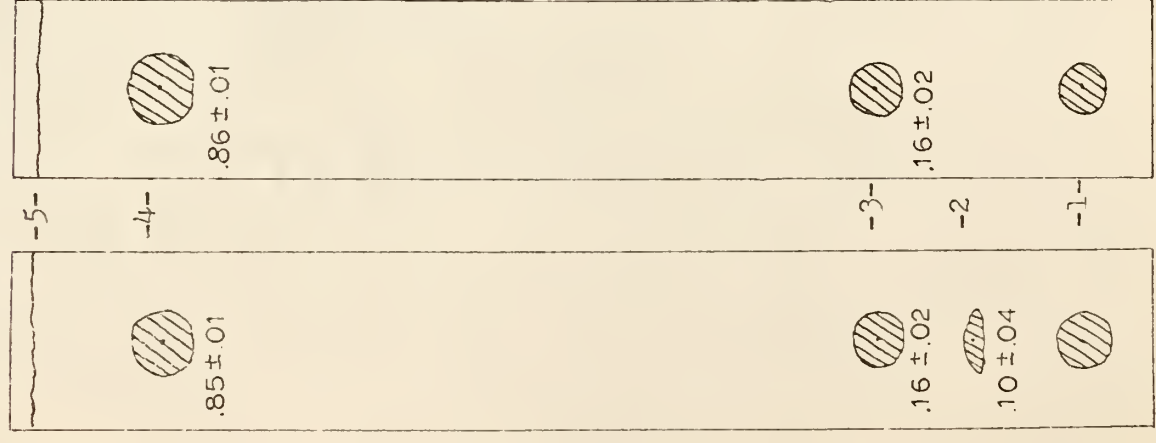


Fig. 14

Fig. 15.

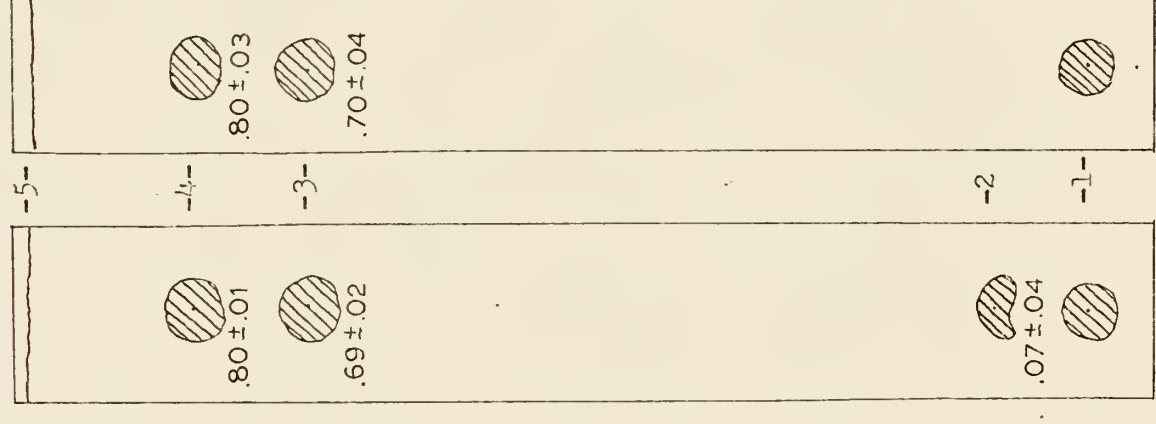


Fig. 15

Thin layer chromatography of diazinon and breakdown products on leaves and glass plates after exposure to sunlight, artificial sunlight, near and far ultraviolet, and infrared.

The tlc plates were coated with cellulose; immobile phase, 20% dimethyl formamide in acetone; mobile phase, iso-octane; development, bromine fluorescein silver nitrate reagent.

1. Solvent origin
2. Unknown
3. Diazoxon
4. Diazinon
5. Solvent front

Mean R<sub>f</sub> value and standard deviation.

Paper chromatograms were Whatman No. 1 strips; mobile phase, 25% NH<sub>4</sub>OH in iso-prop-anol; development, Hanes-Isherwood reagent.

1. Ortho phosphate
2. Unknown
3. Diethyl phosphoric acid
4. Diethylthio phosphoric acid
5. Solvent front

(No. 3) was present at 12 and 24 hours under near and far ultraviolet and persisted from three through 12 hours under infrared. This compound was not detected in the less energetic artificial sunlight until the third day and was present until the seventh day. The compound tentatively identified as monoethyl phosphate was not detected under artificial sunlight but was detected under the other light sources. Ortho phosphate (No. 1) was the last product detected in all four light sources and seemed to be the most stable degradation product found in paper chromatography of diazinon. The comparison of paper chromatographic results of artificial sunlight, infrared, and near and far ultraviolet indicated the presence of the same compounds only at different time intervals and for different lengths of persistence. The infrared indicated the phosphoric acid esters of diazinon at an earlier time interval than the other three light sources and also exhibited a greater rate of dissipation than either of the ultraviolet sources or the artificial sunlight. The more energetic light sources of infrared and far and near ultraviolet accelerated the formation of the four phosphoric acid esters which were present. A comparison of the five light sources indicated the infrared, far and near ultraviolet were the most active followed by the artificial sunlight and the no light control. No hydrolysis products were found in the control rinses of plates held in the dark.

Diazinon degradation products and possible breakdown routes. In the removal of diazinon from the glass plates exposed to near and far ultraviolet and infrared it was observed that the 14 day residue was of a cloudy appearance and could not be dissolved with the ethanol rinse. It was finally removed with water indicating degradation of diazinon and

its intermediate products to very water soluble substances. This material could not be detected by tlc or paper chromatograms indicating the extensive nature of the degradation, and the possible formation of new products from the pyrimidinol ring and phosphoric acid. The energy levels of the light sources were reflected in the time required for the detection of diazoxon. Diazoxon was detected at the fifth day in the growth chamber, at the third day under artificial sunlight, at the second day under field conditions, and in the green house, at 24 hours in direct sunlight, and at three hours in the infrared and under near and far ultraviolet. Paper chromatographic results of diazinon support the thin-layer finding in relation to the general energetic activity levels of the four individual light sources tested. The relative activity or energy availability of the light sources tested based upon number of breakdown products in the least amount of time are: infrared, near and far ultraviolet, direct sunlight, green house irradiation, field condition light, artificial sunlight, growth chamber light and no light. A probable degradation scheme indicating the routes the thin-layer and paper chromatographic identified compounds could have followed is presented in Fig. 16. Diazinon was subject to photo-induced oxidation and the result was the formation of diazoxon. Diazinon could be hydrolyzed to form pyrimidinol and diethyl phosphorothioate. The diethyl phosphorothioate could be oxidized to the diethyl phosphate and then hydrolysis of this product to the monoethyl phosphate and ortho phosphate. Diazoxon could also undergo hydrolysis to pyrimidinol and diethyl phosphate. The diethyl phosphate could be hydrolyzed following the same pathway as previously mentioned. The S-ethyl isomer of diazinon could be formed by photo-irradiation of the parent compound. This degradation pathway or scheme of events would explain the breakdown products observed in the preceeding light tests.

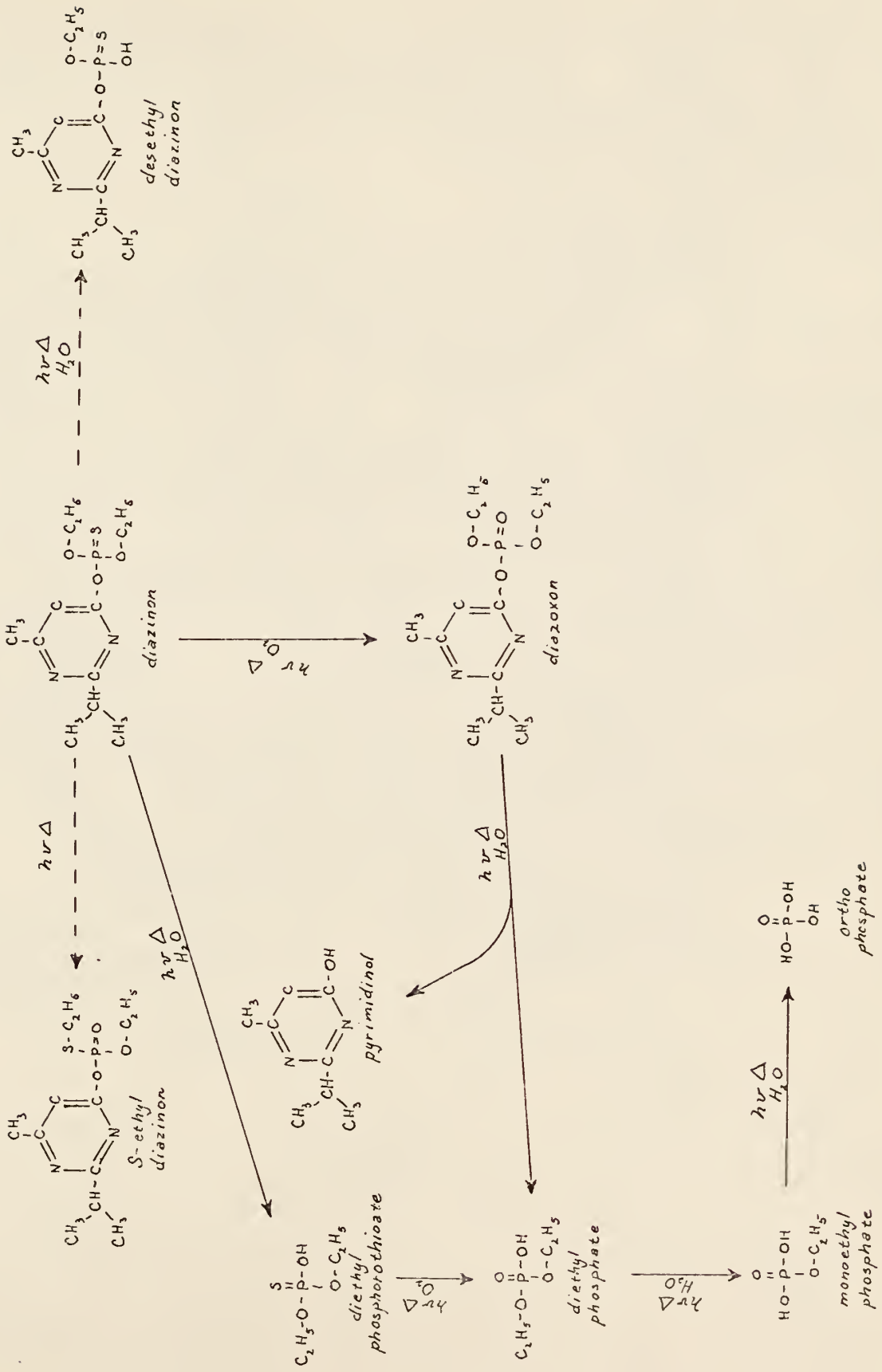


Fig. 16

Parathion Degradation on Glass and Leaf Surfaces  
from Light Exposure

Parathion exposure in the growth chamber. Thin-layer chromatographic results of parathion in the growth chamber on bean leaf and glass plate surfaces are presented in Table 25. Six tlc spots other than the parent compound were formed; four unknown compounds (No. 1, 2, 5, and 6), and p-nitrophenol and paraoxon as illustrated in Fig. 17. Paraoxon was the first breakdown product detected on glass and leaf surfaces and was followed by the appearance of p-nitrophenol. On the seventh day the four unknown compounds were detected on the leaf surfaces. The glass surface indicated the presence of all seven compounds on the ninth day. Unknowns (No. 5 and 6) could possibly be the S-ethyl, S-phenyl parathion, or amino parathion because they are less polar than paraoxon but more polar than parathion. The detection spray reagent of alcoholic KOH indicated the four unknown spots contained the p-nitrophenol moiety. Parathion was present in every sample taken but could not be detected at 17 days. Treated glass and leaf surfaces which were placed in an enclosure containing no light showed no breakdown products at the intervals sampled.

Parathion exposure in the green house. Thin-layer chromatographic results of the exposure of parathion in the green house are presented in Table 26. Paraoxon (No. 4) appeared on the bean and glass surfaces at 24 hours and persisted with the presence of parathion until the seventh day. Unknown (No. 2), p-nitrophenol, and paraoxon appeared at 24 hours on the glass plates and at 48 hours on the bean leaf surface. Unknowns (No. 1 and 5 and 6) were all present on the glass surfaces at two days

Table 25. Parathion exposure on bean leaves and glass plates in the growth chamber ( $26^{\circ}\text{C}$ ,  $40 \pm 5\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time (days)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)						
		Spots as indicated by tlc <u>1/</u>						
		1	2	3	4	5	6	7 <u>2/</u>
1	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
2	Leaf	-	-	-	+	-	-	+
	Glass	-	-	-	+	-	-	+
3	Leaf	-	-	-	+	-	-	+
	Glass	-	-	-	+	-	-	+
5	Leaf	-	-	+	+	-	-	+
	Glass	-	-	+	+	-	-	+
7	Leaf	+	+	+	+	+	+	+
	Glass	+	-	+	+	-	-	+
9	Leaf	+	+	+	+	+	+	+
	Glass	+	+	+	+	+	+	+
12	Leaf	+	+	+	+	+	+	+
	Glass	+	+	+	+	+	+	+
14	Leaf	+	-	+	+	+	-	+
	Glass	+	-	-	+	-	-	+

1/ Numbers correspond to spots in Fig. 17.

- 2/
1. Unknown
  2. Unknown
  3. p-nitrophenol
  4. Paraoxon
  5. Unknown
  6. Unknown
  7. Parathion

Table 26. Parathion exposure on bean leaves and glass plates in the green house ( $16-30^{\circ}\text{C}$ ,  $75 \pm 20\%$  r.h., 16-hours of light and 8-hours of darkness, and light intensity of 2,500 foot candles).

Time	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)						
		Spots as indicated by tlc <u>1/</u>						
		1	2	3	4	5	6	7 <u>2/</u>
1 Hour	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
2 "	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
6 "	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
12 "	Leaf	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	+
24 "	Leaf	-	-	-	+	-	-	+
	Glass	-	+	+	+	-	-	+
2 Days	Leaf	+	+	+	+	-	-	+
	Glass	+	+	+	+	+	+	+
4 "	Leaf	+	+	+	+	+	+	+
	Glass	+	+	+	+	+	+	+
5 "	Leaf	+	+	+	+	+	+	+
	Glass	+	+	+	+	+	+	+
7 "	Leaf	+	+	+	+	+	-	+
	Glass	+	+	+	+	+	-	+
14 "	Leaf	+	-	-	-	-	-	-
	Glass	+	-	-	-	-	-	-

1/ Numbers correspond to spots in Fig. 17.

- 2/
1. Unknown
  2. Unknown
  3. p-nitrophenol
  4. Paraoxon
  5. Unknown
  6. Unknown
  7. Parathion

and appeared on the leaf surfaces 24 hours later. The only breakdown product detected at 14 days was an unknown(s) at the origin. The results obtained in the green house and growth chamber indicated that parathion degradation generally produces compounds which are more polar than the parent compound.

Parathion exposure to direct sunlight. Thin-layer chromatographic results of parathion exposure on glass and leaf surfaces are presented in Table 27. Paraoxon was found on glass and the bean leaves at 12 hours and persisted until termination of the experiment. Glass plates first indicated the presence of *p*-nitrophenol at 24 hours; this same compound was not detected on the leaf surface until 24 hours later. Unknown (No. 1) which the test results of the growth chamber and green house indicated to be the most stable degradation product formed, appeared at 48 hours in both surfaces and persisted until the termination of the experiment. The unknowns (No. 1, 2, 5, and 6) were present on both surfaces at 96 hours. The results of the exposure of parathion to direct sunlight indicated the breakdown products first appeared on the glass plates and then on the bean leaf surface. This observation was essentially the same finding that was observed in the green house tests. A control experiment consisting of treated leaves and glass plates in a chamber containing no light produced no spots other than the parent compound. The direct sunlight control of untreated leaves and glass plates produced spots but they did not have comparable  $R_f$  values of any parathion breakdown product detected.

Table 27. Parathion exposure on bean leaves and glass plates in the direct sunlight (15-30°C, 50  $\pm$  10% r.h., 16-hours of light and 8-hours of darkness, and light intensity of 10-13,800 foot candles).

Time (hours)	Exposure surface	Presence of compounds indicated by (+) and absence indicated by (-)							
		Spots as indicated by tlc <u>1/</u>							
		1	2	3	4	5	6	7	<u>2/</u>
1	Leaf	-	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	-	+
2	Leaf	-	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	-	+
6	Leaf	-	-	-	-	-	-	-	+
	Glass	-	-	-	-	-	-	-	+
12	Leaf	-	-	-	+	-	-	-	+
	Glass	-	-	-	+	-	-	-	+
24	Leaf	-	-	-	+	-	-	-	+
	Glass	-	-	+	+	-	-	-	+
48	Leaf	+	-	+	+	-	-	-	+
	Glass	+	+	+	+	+	-	-	+
96	Leaf	+	+	+	+	+	+	+	+
	Glass	+	+	+	+	+	+	+	+

1/ Numbers correspond to spots in Fig. 17.

- 2/
1. Solvent origin
  2. Unknown
  3. p-nitrophenol
  4. Paraoxon
  5. Unknown
  6. Unknown
  7. Parathion

Parathion exposure on glass plates in the light chamber. Thin-layer chromatographic results of parathion exposure to the five previously mentioned light sources are presented in Table 28. Seven spots were detected by thin-layer chromatography as illustrated in Fig. 17. The four light sources indicated parathion persistence was the greatest under the artificial sunlight followed by near ultraviolet, far ultraviolet, and infrared. This observation is what one would expect considering the thermal and photon emitting capabilities of the four light sources. Compounds (No. 5 and 6) which as previously indicated were thought to be the S-phenyl and S-ethyl isomers of parathion or the aminophenol, were readily detected at one day in the infrared. This would be expected of parathion and all phosphorothioates since isomerization is particularly liable to occur upon heating or exposure to a high energy source of photons. These two compounds were not detected until the fourth and fifth day under artificial sunlight. Paraoxon and unknown (No. 1) were detected the longest time interval of any of the breakdown products under the four light sources. The presence of p-nitrophenol was usually detected with or after the appearance of paraoxon, suggesting the possibility of a degradation route from paraoxon to p-nitrophenol. It could also be possible that parathion was hydrolyzed with the resulting products being diethyl phosphorothioate and p-nitrophenol. The tlc parathion results of the four light sources indicate that the infrared was the most active light source followed by far ultraviolet, near ultraviolet, and artificial sunlight. The parathion control exhibited one noticeable change and that was the presence of paraoxon in the 14 day sample, indicating that parathion in the presence of atmospheric oxygen in a dark environment will convert to its oxygen analog.

Table 28. Parathion exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <u>2/</u>	Time (days)	Spots as indicated by tlc <u>1/</u>						
		1	2	3	4	5	6	7
A	1	+	-	+	+	+	-	+
	2	+	+	+	+	+	+	+
	3	+	+	+	+	+	+	+
	4	+	+	+	+	-	-	-
	5	+	-	+	+	-	-	-
	7	+	-	-	-	-	-	-
	14	-	-	-	-	-	-	-
B	1	+	-	+	+	+	-	+
	2	+	+	+	+	+	+	+
	3	+	+	+	+	-	-	-
	4	+	-	+	+	-	-	-
	5	+	-	-	-	-	-	-
	7	+	-	-	-	-	-	-
	14	-	-	-	-	-	-	-
C	1	-	-	-	-	-	-	+
	2	-	-	-	+	-	-	+
	3	-	-	+	+	-	-	+
	4	+	+	+	+	+	+	+
	5	+	+	+	+	+	+	+
	7	+	+	+	+	-	-	-
	14	+	-	-	-	-	-	-
D	1	+	+	+	+	+	+	+
	2	+	-	-	-	-	-	-
	3	+	-	-	-	-	-	-
	4	+	-	-	-	-	-	-
	5	+	-	-	-	-	-	-
	7	-	-	-	-	-	-	-
	14	-	-	-	-	-	-	-
E	1	-	-	-	-	-	-	+
	2	-	-	-	-	-	-	+
	3	-	-	-	-	-	-	+
	4	-	-	-	-	-	-	+
	5	-	-	-	-	-	-	+
	7	-	-	-	-	-	-	+
	14	-	-	-	+	-	-	+

- 1/
1. Solvent origin
  2. Unknown
  3. p-nitrophenol
  4. Paraoxon
  5. Unknown
  6. Unknown
  7. Parathion

- 2/
- A Near ultraviolet
  - B Far ultraviolet
  - C Artificial sunlight
  - D Infrared
  - E Control or absence of all light

Numbers correspond to spots in Fig. 17.

Paper chromatographic results of parathion exposure to the five light sources are presented in Table 29. The paper chromatograms were developed using the Hanes-Isherwood spray reagent (see Fig. 18) and four breakdown products were detected. Ortho phosphate, diethyl phosphate, diethyl phosphorothioate, and an unknown, thought to be monoethyl phosphate, were identified as breakdown products of parathion by comparison with known standards. Observations indicated that the paper chromatographic results of the far and near ultraviolet were almost the same. The only difference was the presence of compound (No. 2) at one day in the far ultraviolet and this compound was absent at one day under near ultraviolet. Unknown (No. 2) which exhibited a spot at  $R_F$  .08 had an intermediate polarity between ortho phosphate and diethyl phosphate and this is where one would expect the monoethyl phosphate. This unknown  $R_F$  also compared favorably to the  $R_F$  of a similar phosphate, monomethyl phosphate ( $R_F$  .07). The only product detected at seven days in far and near ultraviolet and the infrared was ortho phosphate indicating this compound may be the stable degradation end product of parathion. The comparison of paper chromatographic results of artificial sunlight, infrared and near and far ultraviolet indicated the presence of the same compounds only at different time intervals and at different lengths of persistence. The infrared indicated the phosphate esters of parathion at an earlier time than the other three light sources; this light source also exhibited greater rate of disappearance than either of the ultraviolet sources or the artificial sunlight. The more energetic light sources accelerated the formation of the four compounds indicated to be present. The comparison of the five light sources indicated the infrared

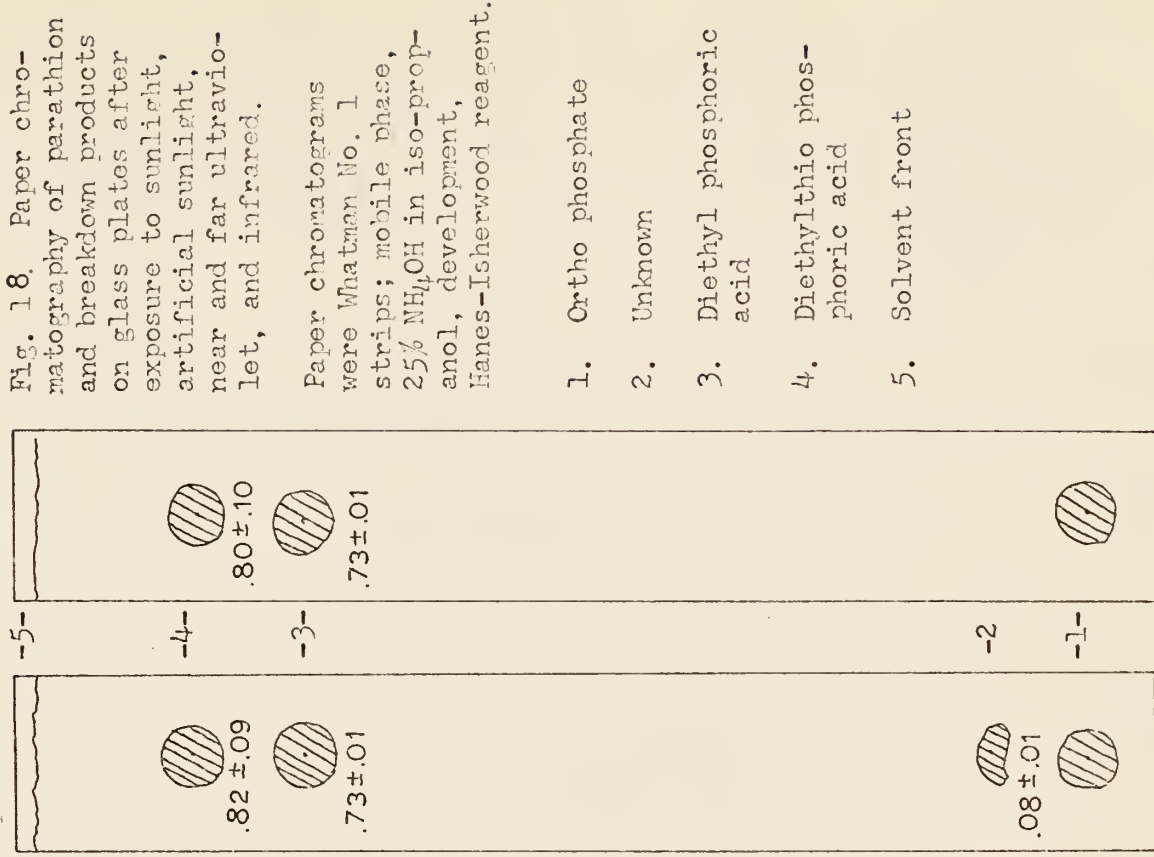
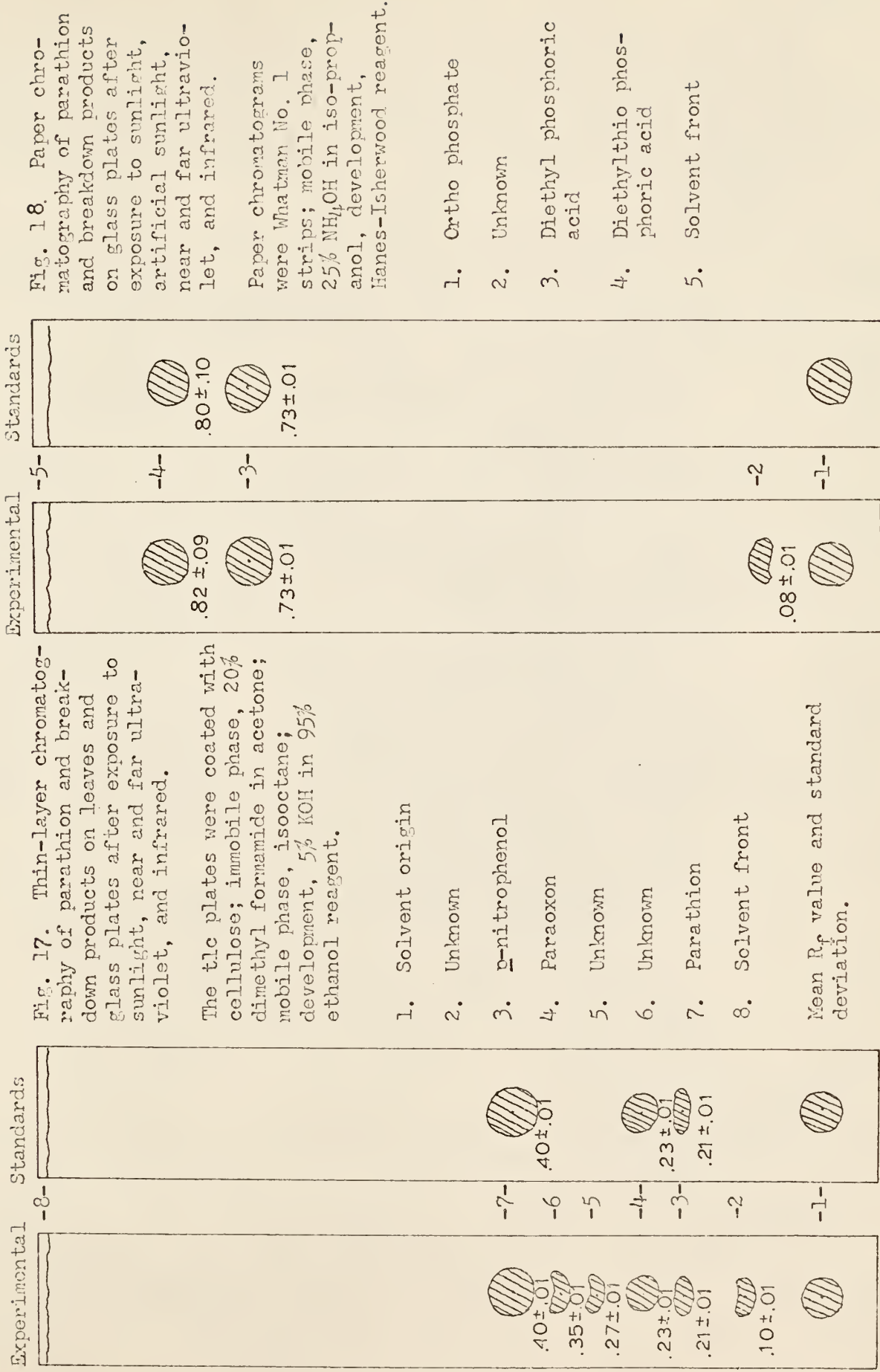
Table 29. Parathion exposure on glass plates in the light chamber (26°C, 40 ± 5% r.h., 24-hours of light and 0-hours of darkness, for light intensity see Table 2). Presence of compounds indicated by (+) and absence indicated by (-).

Light source <u>2/</u>	Time (days)	Spots as indicated by paper chromatography <u>1/</u>			
		1	2	3	4
A	1	+	-	+	+
	2	+	+	+	+
	3	+	+	+	+
	4	+	+	+	+
	5	+	+	+	+
	7	+	-	-	-
	14	-	-	-	-
B	1	+	+	+	+
	2	+	+	+	+
	3	+	+	+	+
	4	+	+	+	+
	5	+	+	+	+
	7	+	-	-	-
	14	-	-	-	-
C	1	-	-	-	-
	2	+	-	-	-
	3	+	+	+	+
	4	+	+	+	+
	5	+	+	+	+
	7	+	-	+	+
	14	-	-	-	-
D	1	+	+	+	+
	2	+	+	+	+
	3	+	-	-	-
	4	+	-	-	-
	5	+	-	-	-
	7	+	-	-	-
	14	-	-	-	-
E	1	-	-	-	-
	2	-	-	-	-
	3	-	-	-	-
	4	-	-	-	-
	5	-	-	-	-
	7	-	-	-	-
	14	-	-	-	-

- 1/
1. Ortho phosphate
  2. Unknown
  3. Diethyl phosphoric acid
  4. Diethylthio phosphoric acid

- 2/
- A Near ultraviolet
  - B Far ultraviolet
  - C Artificial sunlight
  - D Infrared radiation
  - E Control or no light

Numbers correspond to spots in Fig. 18.



and far ultraviolet to be most active followed by the near ultraviolet, artificial sunlight, and no light. The control or no light exposure exhibited no spots when sprayed with Hanes-Isherwood reagent.

Parathion degradation products and possible breakdown routes. The thin-layer chromatoplates were sprayed with alcoholic KOH which detects the p-nitrophenol moiety and thus is used for detection of parathion and its oxon and any p-nitrophenol containing metabolites. The paper chromatograms were sprayed with Hanes-Isherwood reagent which detects the phosphate esters and ortho phosphates. In the removal of parathion from the glass plates it was observed that the insecticide was not sprayed as a continuous film, but rather existed in the same form of small droplets as was exhibited by the other three phosphorothioates tested. The color of the parathion glass plate residue rinses ranged from pale yellow to dark yellow to brown. The color of the residue depended upon the type and duration of light exposure. The energy levels of the light sources were reflected in the time required for the detection of paraoxon. Paraoxon was detected on the second day in the growth chamber and under artificial sunlight, at one day in the near and far ultraviolet, green house and infrared, and at 12 hours in the direct sunlight. The paper chromatographic results support or indicate the same findings in relation to the general energy levels of the light sources as were found in tlc results. The relative activity or energy availability of the light sources, based upon number of breakdown products indicated in the least amount of time, indicates direct sunlight, green house sunlight, infrared, and far ultraviolet to be the most energetic. However, infrared and ultraviolet were

not sampled at periods under one day and since they were detected at one day it is possible their appearance could have been at a much earlier time period. The other light sources listed in decreasing order of energy are: near ultraviolet, artificial sunlight, growth chamber light, and no light. A possible degradation scheme indicating the routes the tlc and paper chromatographic identified compounds could have followed is presented in Fig. 19. Parathion was subject to photo-induced oxidation and thus the oxon was formed. This oxon could be hydrolyzed to the p-nitrophenol and the diethyl phosphate. Parathion can undergo hydrolysis and form p-nitrophenol and diethyl phosphorothioate and the phosphorothioate can oxidize to the diethyl phosphate. The diethyl phosphate can undergo hydrolysis to the monoethyl phosphate and subsequent ortho phosphate. The p-nitrophenol can be reduced to p-aminophenol. The S-phenyl and S-ethyl parathion can be formed by photoirradiation of the parent compound. This degradation scheme of events would explain the breakdown products which were observed in the light experiments.

#### Insecticide Exposure to Various Light Combinations

Insecticide exposure to the combination of light sources. The combination of the two light sources near and far ultraviolet upon the malathion, Guthion, methyl parathion, parathion and diazinon proved to be no different than the singular action of the far ultraviolet. The combination of near ultraviolet, artificial sunlight, and infrared produced results identical to the ones obtained from the single exposure tests of infrared upon the five organophosphorus insecticides. The infrared and far ultraviolet were the two most energetic light sources in each of the two

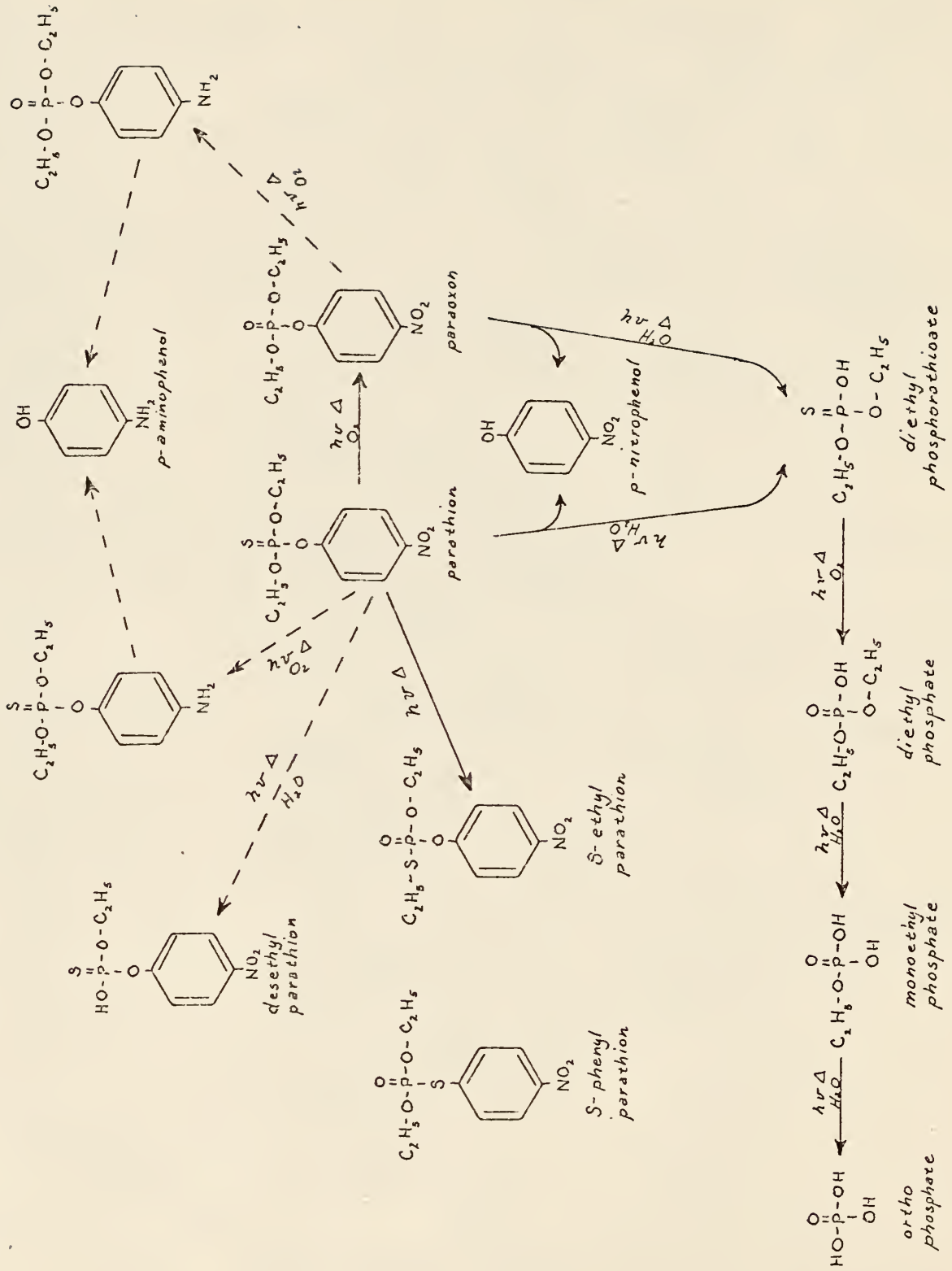


Fig. 19

combinations, and the rate of degradation on the five insecticides closely followed their characteristic pattern of degradation when they acted upon these compounds independently.

## SUMMARY AND CONCLUSIONS

### Light Induced Degradation Reactions

The five organophosphorus insecticides investigated can be divided into two groups, the dimethyl compounds which include malathion, methyl parathion, and Guthion, and the diethyl compounds of parathion and diazinon.

Oxidation. The first light induced reaction which was detected in all the insecticides tested was the oxidation of the thiono group ( $P=S$ ) to the corresponding phosphate groups ( $P=O$ ). Oxidation of thiophosphorus insecticides has been reported by several investigators. El-Refai (1960) investigating the effects of ultraviolet light upon malathion reported the material resulting from exposure was malaoxon as well as other oxidation and degradation products. Frawley et al. (1958) exposed parathion to near ultraviolet light and the material resulting was a mixture of parathion, paraoxon and other oxidation and degradation products. Infra-red and far ultraviolet caused the conversion of the thiophosphorus insecticides to the  $P=O$  most readily. McPherson and Johnson (1956) reported that prolonged heating of the methyl analog of parathion and similar phosphorothioates can lead to extensive oxidation. The infrared exposure tests in this study indicated extensive degradation took place most rapidly and it was thought this rapid degradation was due in part

to the high temperatures (38-49°C) exhibited by the infrared. The near ultraviolet exposure also indicated the presence of the oxons but generally at later time intervals than the infrared. Artificial sunlight exposure was the least energetic of the light chamber tests.

Isomerization. Several unknown breakdown products which had an intermediate polarity between the parent compound and the oxon were detected and these compounds were thought to be the isomers of the parent compounds. El-Refai and Hopkins (1966) investigating parathion found the S-ethyl isomer of parathion exhibited an intermediate polarity which corresponded to the approximate  $R_f$  value detected in the light exposure observations of parathion. One unknown compound was detected in the malathion residues at an  $R_f$  which indicated an intermediate polarity between the parent compound and the oxon. El-Refai (1960) observed several compounds to be present after ultraviolet exposure and they exhibited the same polarity as the unknown product detected. Three breakdown products were observed at an  $R_f$  value between the methyl parathion and its oxon. These could possibly be the S-methyl, S-phenyl, or p-aminophenol, but further investigation is needed before a positive identification can be made. Metcalf and March (1953) described chromatographic studies conducted on the thermal decomposition products of methyl parathion and indicated the presence of four compounds, two of which were O,S-dimethyl O-(p-nitrophenyl) phosphorothic acid and dimethyl p-nitrophenol phosphate. Sandi (1958) investigated the effects of ultraviolet light on solutions of parathion and found several breakdown products. One of these decomposition products was proposed to be p-aminophenol. Guthion exhibited a spot which was of intermediate polarity

between the oxon and the parent compound; this is where one would expect the S-methyl isomer of Guthion. Only one of the two diethyl phosphorus insecticides examined had tlc spots which would correspond to the area where one would expect to find the isomers. Parathion exhibited two unknown spots in this area of intermediate polarity between the parent compound and the oxon. The two spots were thought to possibly be the S-ethyl, S-phenyl or *p*-aminophenol. Schrader (1942) referring to the heat isomerization of parathion at 130° to 140°C stated that the S-ethyl isomeride was one of the decomposition products detected and this product was less polar than the parent compound. The diazinon did not exhibit any spots in this area which could be interpreted as its isomerization products.

Hydrolysis. O'Brian (1960) stated the phosphates (P=O) are less stable to hydrolysis than the thiophosphorus insecticides (P=S) and as such are more capable of hydrolytic reactions. The dimethyl phosphorus insecticides were hydrolyzed to the phosphoric acid esters of dimethyl phosphoro dithioate, dimethyl phosphorothioate, dimethyl phosphate, monomethyl phosphate and ortho phosphate. Hydrolytic products of organophosphorus insecticides were previously reported by several investigators. Shipp (1963) tentatively identified dimethyl phosphorothioate and dimethyl phosphate as breakdown products of sunlight decomposition of methyl parathion on cotton leaves. Tomizawa and Sato (1960) reported that dimethyl dithiophosphate was present in and on rice plants which were previously treated with malathion. Dimethyl phosphorothioate was observed in Guthion and malathion since both were phosphorodithioates this was to

be expected. The diethyl phosphorus insecticides also readily underwent hydrolysis and diethyl phosphorothioate, diethyl phosphate, and ortho phosphate were detected. An unknown was detected which could have been the monomethyl phosphate, because its  $R_f$  was close to the origin. El-Refai (1960) reported the monomethyl phosphate to be highly polar and having a low  $R_f$  in the tlc chromatograms employing the normal phase of development. The hydrolytic products of dimethyl and diethyl phosphates were observed to follow the general scheme of degradation from the dimethyl or diethyl phosphates to the monomethyl or monoethyl phosphate to ortho phosphate. This hydrolysis scheme would account for the persistence which was observed at various time intervals of each of the phosphoric acid esters, and is especially true of the ortho phosphate which is the stable end product of phosphoric ester hydrolysis. This product was the last hydrolytic product to be observed in most of the light exposure tests. It was observed that other hydrolysis products could occur in the photochemical degradation of the organophosphorothioate insecticides as previously reported by several investigators. Rowlands (1965) reported that when malathion treated wheat and maize was stored in sealed jars for six months and analyzed monthly, malathion di acid and malathion mono acid were identified by tlc to be present. The tlc results of malathion indicated an unknown material was present at the point of origin and this could possibly be the hydrolysis product(s), malathion mono or di acid. Diazinon also indicated the presence of an unknown compound which could have possibly been a pyrimidinol derivative. A pyrimidinol derivative was proposed as a breakdown product by Kanschuh and Hopkins (1968) in their investigation of the absorption,

translocation, and metabolism of diazinon in bean plants. Ralls et al. (1966) studied the fate of radioactive diazinon of field grown crops and found only one degradation product diazoxon but proposed that diazinon was oxidized to oxo-diazinon which was, in turn hydrolyzed to 2-isopropyl-4-methylpyrimidin-6-ol. Parathion and methyl parathion indicated the occurrence of p-nitrophenol and this breakdown product was also reported by El-Refai and Hopkins (1966) in their investigation of the parathion deposits on bean and glass surfaces in a semicontrolled environment.

Direct sunlight, green house light, infrared and far and near ultraviolet were the most energetic light sources tested. Artificial sunlight, growth chamber light and no light were the least active light sources. The usefulness of thin-layer and paper chromatography as a means of identifying organophosphorus compounds has proven to be a valuable qualitative tool, however, the problem of positive identification of photo-induced residues still remains to be solved. This could be accomplished by further quantitative analysis using ultraviolet or infrared spectroscopy.

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PHOTODEGRADATION OF FIVE ORGANOPHOSPHORUS INSECTICIDES  
ON GLASS AND LEAF SURFACES

by

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AN ABSTRACT OF A MASTER'S THESIS

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Five organophosphorus insecticides, malathion, Guthion, methyl parathion, parathion and diazinon, containing the thiono sulfur group (P=S) were applied to glass and bean leaf surfaces and immediately exposed to growth chamber light, green house sunlight, and direct sunlight. The glass plates and bean leaves were removed after exposure at intervals between 1-14 days from the growth chamber and green house, and from direct sunlight at intervals between 1-96 hours. The insecticide residues were rinsed from the surfaces and analyzed by thin-layer chromatography (tlc). The TLC results indicated the organothiophosphates undergo several degradation reactions including photo-oxidation, isomerization, and hydrolysis.

The oxygen analogs of all five insecticides were the first degradation products detected and persisted or were continually being formed from the parent insecticide as long as the latter persisted. Photo-oxidation is therefore one of the initial and most important degradation reactions.

Photo-induced isomerization to the S-alkyl derivatives was indicated because the certain TLC spots detected were more polar than the parent compounds and less polar than the corresponding oxygen analogs. The persistence of these unknown compounds was short and their appearance was detected only under the more energetic light sources.

Evidence of hydrolysis was observed in methyl parathion and parathion with the detection of *p*-nitrophenol, and in malathion by TLC spots thought to be the mono and dicarboxylic acid hydrolytic products. Diazinon also exhibited a spot which was thought to be the pyrimidinol hydrolysis product. The light source producing the most degradation products in the least amount of time was direct sunlight followed by green house and growth chamber light. Diazinon and methyl parathion applied as an aerial

spray to field corn were also analyzed at daily intervals for 18 days. The breakdown products detected from both insecticides were the same compounds found in the green house, direct sun, and growth chamber tests. Methyl parathion persisted until the ninth day and diazinon until the seventh day and their corresponding oxons until the tenth and ninth day.

The five insecticides were also applied to the surface of glass plates and exposed in light chambers to near ultraviolet, far ultraviolet, infrared, artificial sunlight, and no light at time intervals ranging from one hour to 14 days. The exposed plates were removed from the light chamber and the residue was collected and analyzed by tlc and paper chromatography. The same degradation products that were observed in the previous tests were detected in the residues obtained from the light chamber tests. Photo-induced oxidation, isomerization and hydrolysis of the parent organothiophosphorus were the principle degradation reactions under the different light sources. No degradation was observed in the absence of light except the formation of the oxygen analogs at the 14 day interval. The time involved in breakdown product formation was dependent upon the energy level of the light source. The tlc results indicated that decomposition and disappearance of the insecticides and their degradation products occurred most readily under the heat producing infrared. The next most active light sources were far ultraviolet, near ultraviolet, and artificial sunlight.

Paper chromatograms developed with Hanes-Isherwood reagent revealed the presence of phosphate ester hydrolysis products. The presence of dimethyl phosphorodithioate was indicated in the residues of Guthion and malathion. The next products detected were dimethyl phosphorothioate

followed by dimethyl phosphate, monomethyl phosphate and ortho phosphate. Methyl parathion followed the same degradation scheme with the exclusion of dimethyl phosphorodithioate, since it was not a phosphorodithioate. Parathion and diazinon indicated the presence of diethyl phosphorothioate, followed by diethyl phosphate and ortho phosphate. An unknown phosphoric acid ester was detected at  $R_f$  .07 and this was thought to be the monoethyl phosphate. Phosphoric acid esters were hydrolyzed most readily under infrared. Far and near ultraviolet were the next most energetic light sources followed by artificial sunlight. Degradation to the stable ortho phosphate was observed in all five of the thiophosphates.





